VOL. XVI. [JANUARY, 1894.] No. 1.

AMERICAN CHEMICAL JOURNAL.

ON THE COMBINATION OF SULPHURIC ACID WITH WATER IN THE PRESENCE OF ACETIC ACID.

BY HARRY C. JONES.

The strong attraction of sulphuric acid for water is utilized daily for the purpose of removing water from other substances. Not only is the qualitative fact established, but certain definite compounds of water with the acid have been isolated. The ordinary acid is but the first hydrate, containing one molecule of water to one of sulphur trioxide, $O_3S.H_2O$. A second hydrate containing two molecules of water is also known, $OS(OH)_4 = O_3S.2H_2O$. Other hydrates containing a much larger number of molecules of water have been thought to be probable from a study of certain physical properties of the solutions of sulphuric acid in water.

Quantitative measurements of the amounts of heat evolved when sulphuric acid is added to water in varying proportions, have been made by Hess, Favre and Silbermann and others, but probably the most accurate work has been done by Julius Thomsen.[1] He has found that the amount of heat liberated when the two are brought together in the proportion of one molecule of sulphuric acid to one molecule of water, is about one-third of the total heat set free when almost an unlimited amount of water (1599 molecules) is added to the sulphuric acid; further, that about one-half of the total heat is liberated when the two are mixed in the proportion of one molecule of acid to two of water.

[1] Ber. d. chem. Ges. **3**, 498; and Thermochem. Untersuch., Bd. **3**, 44.

These results show at least that the amount of energy which appears as heat on the addition of a molecule of water is much greater for the first than for the second molecule, and this amount decreases rapidly with increase in the quantity of water.

Mendeléeff[1] has studied Thomsen's data for the heat of solution, and Marignac's for the specific heat of the solutions, and has pointed out that the maximum amount of heat for say 100 volumes of the solution, and the maximum increase in temperature when water and sulphuric acid are mixed, correspond very closely to the proportions which would form the trihydrate $H_2SO_4.2H_2O = S(OH)_6$. He also states[2] that the maximum contraction nearly corresponds to these same proportions.

He has also studied[3] the specific gravity determinations of solutions of sulphuric acid in water, measurements of which have been made by Lunge, Marignac, Mendeléeff, Ostwald, Schertel, Winkler and others. From these it appears that the changes in the differential quotient $\frac{ds}{dp}$ indicate the hydrates $SO_3.H_2O$, $SO_3.2H_2O$ and $SO_3.3H_2O$ (p = percentage composition of H_2SO_4). When the percentage composition of solutions of sulphuric acid and the value $\frac{ds}{dp}$ are plotted as a curve, this is stated to indicate, in addition to the above, the hydrates $H_2SO_4.6H_2O$ and $H_2SO_4.150H_2O$.

It can be said in advance that none of these higher hydrates has been isolated, and their existence as definite chemical compounds in solution is far from proven.

While certain definite compounds have been isolated, but little is known of the way in which sulphuric acid combines with water when, *e. g.*, an excess of water is present, or which of the different compounds exists in solution under such conditions. Again, when just one or two equivalents of water are present, is all the water in combination with all the sulphuric acid in these proportions, or does a part of each remain free? It would be of special interest if positive evidence could be furnished that the supposed hydrates, containing a hundred or more molecules of water, were definite chemical compounds existing as such in the solutions. The question of the stability of the different hydrates in solution also arises, as to whether they are capable of existence independent of the solvent, or are dissociated or decomposed by it.

[1] Ber. d. chem. Ges. **19**, 400. [2] *Ibid.* **19**, 387.
[3] *Ibid.* **19**, 379; Ztschr. phys. Chem. **1**, 273; Grundlagen d. Chemie, 923-925.

A satisfactory quantitative study of the combination of sulphuric acid with water seems not to have been made up to the present time, and the above points remain unsettled. To solve this problem, some method must be employed which would enable one to determine the total *number* of molecules present under the varying quantitative conditions in which water and sulphuric acid are brought together. Such a method has been found in the lowering of the freezing-point of the solvent by the dissolved substance. But for this purpose some solvent must be employed on which neither water nor sulphuric acid would act chemically. The only reaction which could then take place would be between the water and the sulphuric acid, and this could be determined by the changes in the freezing-point of the solvent. Such a solvent is pure acetic acid. This has also the special advantage that its freezing-point is in a very convenient position to determine.

The method of work consisted in preparing pure acetic acid and determining its freezing-point, then adding a known amount of water, and determining the lowering produced by this water. A weighed amount of sulphuric acid was then added to another quantity of the acetic acid, and the lowering of the freezing-point produced by the sulphuric acid determined. Finally a known quantity of sulphuric acid was added to acetic acid to which a weighed amount of water had been added, and the lowering produced by both together determined. The same amount of acetic acid was used in every case. We should then know the lowering produced by the water alone, by the sulphuric acid alone, and by both when brought together in the acetic acid, which are the necessary data for determining the state of combination of the sulphuric acid and water, as will be seen.

Two series of determinations, in one of which a very small amount of water was used, and different amounts of sulphuric acid, and in the other, much water and again varying amounts of sulphuric acid, might have been sufficient to show what compounds were formed, but it was also desired to test the stability of these compounds at very different concentrations in the acetic acid, and in the presence of varying amounts of their constituents in excess. Therefore several series of measurements were necessary, using at first very little water, and gradually increasing this from one series to the next, as far as was possible with the thermometer employed. Different amounts of sulphuric acid were added, and

the freezing-points determined. Thus for any given series of measurements, the amount of water remained constant and the quantity of sulphuric acid was varied.

Rüdorff[1] has pointed out that when sulphuric acid is added to acetic acid containing water, the freezing-point is raised. Thus, when 10 parts of water are added to 100 parts of acetic acid the freezing-point is 4.3°. If 20 parts of sulphuric acid are then added, the freezing-point is 10.7°.

Pickering[2] has more recently utilized the same fact to determine, as he thought, whether dissociation takes place in solution. He has stated the problem clearly, and the method at first sight would seem capable of throwing light upon it. The results which he obtained show that the sulphuric acid and water combine to form a smaller number of parts, rather than dissociate into a larger number. From this Pickering argues against the dissociation theory. But when we consider that most of the solutions which he employed were so concentrated that their *conductivity* was almost *zero*, his argument against the theory, based on these results, is without force, since, to state a truism, the theory of electrolytic dissociation applies only to those solutions in which electrolytic dissociation takes place, and this as shown by the conductivity or some other method. He has also made a few determinations employing much less sulphuric acid in proportion to the water and, without determining the conductivity of his solutions, has concluded that the theory must at least apply to these. Had it even been shown that such solutions conduct electricity to some extent, the meagreness of his experimental data from the freezing-point method should have prohibited final conclusions being drawn from them.

Method of Work.

The ordinary Beckmann apparatus and thermometer divided into hundredths of a degree, were employed. It was not practicable to use the large thermometer divided into thousandths of a degree, because the lowerings produced were far too great. Since the acetic acid used as a solvent would take up moisture from the air, the arrangement which has been devised by Beckmann[3] for protecting the solvent from this moisture was employed at first.

[1] Ber. d. chem. Ges. **3**, 393.
[2] *Ibid.* **24**, 1579.
[3] Ztschr. phys. Chem. **7**, 323.

This was not, however, found to be entirely satisfactory, for when only a small amount of sulphuric acid was added to the bulb and a very gentle stream of air passed through the sulphuric acid for a long time, the acetic acid in the apparatus was found to contain a trace of sulphuric acid. The amount of sulphuric acid which was thus carried over mechanically was very small, yet was always found when the stream of air was allowed to flow for a considerable time. The apparatus was, however, found to work perfectly satisfactorily when the air was first passed through a tube containing sulphuric acid and then allowed to enter the apparatus through the side Beckmann bulb which was kept dry. When this device was employed, no sulphuric acid was found in the acetic acid.

The freezing-point of 25 cc. (26.335 grams) of acetic acid was determined by the thermometer, a weighed amount of water was then added and the freezing-point again determined. The difference gave the lowering produced by the water alone. Then weighed amounts of sulphuric acid were added and the freezing-points ascertained. Duplicate determinations were made and the mean taken as the true value.

Preparation of Pure Acetic Acid.

In order that the lowering of the freezing-point produced by sulphuric acid alone could be determined, it was necessary to have acetic acid as free as possible from water. Some difficulty was experienced in preparing such a specimen of acetic acid. The glacial acetic acid of commerce was fractionally recrystallized *thirty-five times*. The product from the last crystallization froze at 16.5° C. and had a specific gravity of 1.0534. This acid, which was used in the following determinations, seemed to be entirely free from any appreciable amount of water: when a drop of sulphuric acid was added it produced a lowering of the freezing-point. During the last three or four crystallizations the freezing-point of the acetic acid did not change to an observable extent. Five or six liters of the commercial acid were used in the first crystallization. From this about 200 cc. of the pure acid were obtained after thirty-five crystallizations. In order to prepare a quantity of acid sufficient for this work the entire process was repeated twice.

Results.

The lowerings of the freezing-point of acetic acid produced by the different amounts of water were determined and plotted as Curve 1, in which the ordinates represent concentrations and the abscissas lowerings of the freezing-point. The unit on the ordinate = 0.04 gram, on the abscissa = 0.2°. The lowering produced by a given amount of water, say a milligram, gradually decreased with increase in the total amount of water present. This is seen in the gradual bending of the curve from the abscissa, and also from the decrease in the molecular lowering (Column 3, Table A). This decrease is far greater than would be caused by the change in volume due to the addition of more and more water. The corresponding results from sulphuric acid have been plotted in Curve 2, in which the ordinate unit = 0.250 gram, and the abscissal unit = 0.2°. The molecular lowering, as calculated, decreases to a minimum and then increases, yet the total volume of the solution is ever increased by the addition of more and more sulphuric acid. From these curves the lowerings of the freezing-point of the acetic acid produced by the different amounts of sulphuric acid alone and water alone, can be read off at once. Each must then be corrected for the increase in volume due to the presence of the other.

Table A gives the gram-molecular lowering for water, B that for sulphuric acid.

TABLE A.

Lowerings of the Freezing-point of Pure Acetic Acid by Small Quantities of Water.

Wt. Water added to 26.335 grams CH_3COOH.	Lowering of the Freezing-point.	Gr.-mol. Low. 18 grams H_2O to 1000 grams CH_3COOH.
0.062 gram	0.480°	3.67
0.130	0.985	3.59
0.204	1.497	3.48
0.275	1.970	3.39
0.349	2.444	3.32
0.417	2.858	3.25
0.531	3.507	3.13
0.637	4.076	3.03
0.716	4.500	2.98
0.807	4.970	2.92

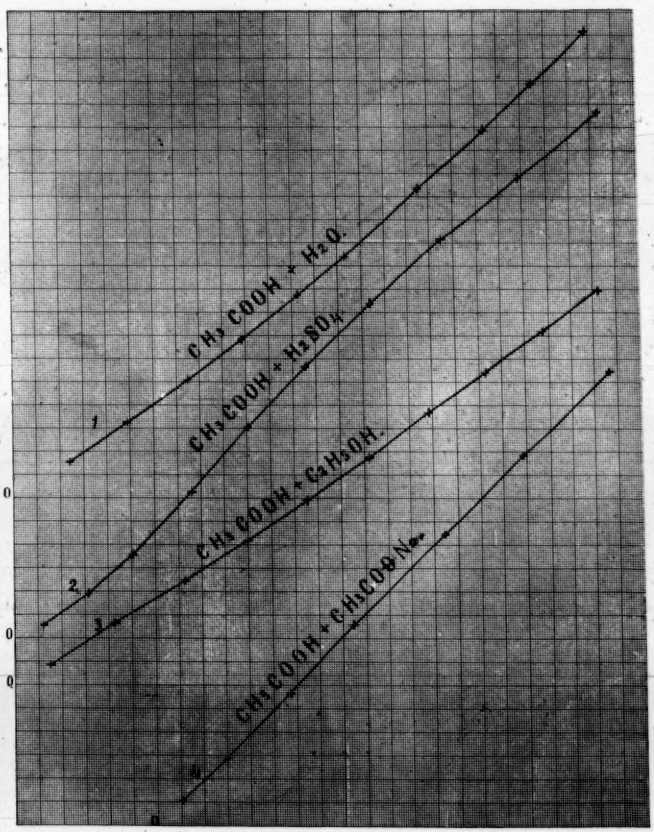

$CH_3COOH + H_2O$.
$CH_3COOH + H_2SO_4$.
$CH_3COOH + C_2H_5OH$.
$CH_3COOH + C_4H_9COONa$
1
2
3
4

TABLE B.

Lowerings of the Freezing-point of Pure Acetic Acid by Small Quantities of Sulphuric Acid.

Wt. Sulphuric Acid to 26.335 grams CH_3COOH.	Lowering of the Freezing-point.	Gr.-mol. Low. 98 grams H_2SO_4 to 1000 grams CH_3COOH.
0.146 gram	0.245°	4.33
0.474	0.630	3.43
0.893	1.015	2.93
1.571	1.521	2.50
2.254	2.005	2.29
2.919	2.505	2.21
3.599	3.075	2.21
4.293	3.700	2.22
4.956	4.385	2.28
5.662	5.065	2.31

Six series of measurements have been made in which both water and sulphuric acid were employed. The amount of water used in the different series varied from 0.068 gram to 0.753 gram, and varying amounts of sulphuric acid were added in each series. The results are given in the following Tables I to VI. Just 25 cc. acetic acid = 26.335 grams were used in each series of measurements. The amount of water used in each series is given in the first line above the table. Column 1 gives the amounts of sulphuric acid which were added to the acetic acid containing the amount of water stated; Column 2, the lowerings of the freezing-point produced by the different amounts of sulphuric acid, as read from the curve and corrected for the increase in volume caused by the presence of the water; Column 3, the lowerings produced by the water as read from the curve and corrected for the increase in volume produced by the sulphuric acid. This value decreases as the increase in sulphuric acid present increases the volume. Column 4 gives the sum of the lowerings of the sulphuric acid and water as thus corrected; Column 5, the lowerings of the freezing-point actually found when the sulphuric acid and water were brought together in the acetic acid; Column 6, the difference between the calculated lowering, if the two did not combine with each other, and the lowering found.

Lowering of the Freezing-point of Acetic Acid by Sulphuric Acid and Water.

Table I.

26.335 grams acetic acid. 0.068 gram water.

Amounts of H_2SO_4 in grams.	Lowering by H_2SO_4.	Lowering by H_2O.	Sum of the last two.	Lowering found.	Difference.
0.088	0.160°	0.540°	0.700°	0.630°	0.070°
0.178	0.290	0.540	0.830	0.760	0.070
0.294	0.430	0.535	0.965	0.820	0.145
0.410	0.550	0.535	1.085	0.870	0.215
0.642	0.800	0.530	1.330	0.950	0 380
0.883	1.000	0.530	1.530	1.060	0.470
1.347	1.360	0.525	1.885	1.280	0.605
2.050	1.870	0.520	2.390	1.740	0.650
3.312	2.830	0.505	3.335	2.658	0.677
4.898	4.340	0.490	4.830	4.110	0.720

Table II.

26.335 grams acetic acid. 0.126 gram water.

Amounts of H_2SO_4 in grams.	Lowering by H_2SO_4.	Lowering by H_2O.	Sum of the last two.	Lowering found.	Difference.
0.092	0.165°	0.950°	1.115°	1.002°	0.113°
0.760	0.895	0.935	1.830	1.106	0 724
1.422	1.415	0.920	2.335	1.392	0.943
2.098	1.900	0.910	2.810	1.792	1.018
2.824	2.440	0.895	3.335	2.300	1.035
3.498	3.000	0.885	3.885	2.832	1 053
4.187	3.600	0.875	4.475	3.447	1.028
4.860	4.280	0.865	5.145	4.074	1.071
5.544	4.960	0.855	5.815	4.749	1.066

Table III.

26.335 grams acetic acid. 0.255 gram water.

Amounts of H_2SO_4 in grams.	Lowering by H_2SO_4.	Lowering by H_2O.	Sum of the last two.	Lowering found.	Difference.
0.108	0.185°	1.860°	2.045°	1.862°	0.183°
0.321	0.455	1.845	2.300	1.750	0.550
0.565	0.705	1 840	2.545	1.655	0.890

Amounts of H_2SO_4 in grams.	Lowering by H_2SO_4.	Lowering by H_2O.	Sum of the last two.	Lowering found.	Difference.
1.029	1.110°	1.815°	2.925°	1.580°	1.345°
1.717	1.620	1.800	3.420	1.690	1.730
2.406	2.100	1.770	3.870	2.013	1.857
3.113	2.655	1.750	4.405	2.470	1.935
3.794	3.230	1.720	4.950	2.955	1.995
4.460	3.830	1.705	5.535	3.565	1.970
5.133	4.515	1.685	6.200	4.230	1.970
5.911	5.230	1.660	6.890	5.080	1.810

Table IV.

26.335 grams acetic acid. 0.496 gram water.

Amounts of H_2SO_4 in grams.	Lowering by H_2SO_4.	Lowering by H_2O.	Sum of the last two.	Lowering found.	Difference.
0.201	0.305°	3.310°	3.615°	2.980°	0.635°
0.651	0.780	3.270	4.050	2.439	1.611
1.331	1.315	3.220	4.535	2.060	2.475
2.055	1.835	3.175	5.010	2.052	2.958
2.744	2.335	3.135	5.470	2.280	3.190
3.403	2.860	3.085	5.945	2.655	3.290
4.095	3.460	3.055	6.515	3.170	3.345
4.808	4.160	3.010	7.170	3.790	3.380
5.497	4.820	2.975	7.795	4.410	3.385
6.190	5.470	2.945	8.415	5.030	3.385

Table V.

26.335 grams acetic acid. 0.728 gram water.

Amounts of H_2SO_4 in grams.	Lowering by H_2SO_4.	Lowering by H_2O.	Sum of the last two.	Lowering found.	Difference.
0.659	0.775°	4.520°	5.295°	3.340°	1.955°
1.367	1.330	4.450	5.780	2.680	3.100
2.056	1.820	4.380	6.200	2.457	3.743
2.752	2.335	4.310	6.645	2.510	4.135
3.676	3.055	4.250	7.305	2.900	4.405
4.354	3.660	4.200	7.860	3.350	4.510
5.050	4.360	4.140	8.500	3.870	4.630
5.728	4.980	4.080	9.060	4.560	4.500
6.187	5.410	4.065	9.475	5.020	4.455

TABLE VI.

26.335 grams acetic acid. 0.753 gram water.

Amounts of H_2SO_4 in grams.	Lowering by H_2SO_4.	Lowering by H_2O.	Sum of the last two.	Lowering as found.	Difference.
0.109	0.185°	4.690°	4.875°	4.474°	0.401°
0.224	0.330	4.670	5.000	4.263	0.737
0.447	0.585	4.645	5.230	3.850	1.380
0.679	0.795	4.615	5.410	3.540	1.870
1.209	1.215	4.565	5.780	3.002	2.778
1.654	1.540	4.545	6.085	2.734	3.351
2.349	2.020	4.475	6.495	2.607	3.888
3.119	2.600	4.410	7.010	2.752	4.258
3.829	3.185	4.345	7.530	3.037	4.493
4.520	3.840	4.295	8.135	3.495	4.640
5.218	4.510	4.235	8.745	4.032	4.713
5.927	5.160	4.190	9.350	4.713	4.637
6.632	5.825	4.130	9.955	5.383	4.572

The results cannot be regarded as very exact, since some small sources of error are unavoidably present in them. Thus, when the lowering of the freezing-point for sulphuric acid as read from the curve was corrected for the increase in volume caused by the presence of the water, this correction was based on the assumption that the water simply played the role of so much more acetic acid. Again, the lowerings produced by the water were corrected for the increase in volume due to the sulphuric acid, on the same assumption for the sulphuric acid. The assumption was exactly this, that a given amount of water would produce the same lowering of the freezing-point, say with 28 cc. acetic acid as with 25 cc. acetic acid and 3 cc. sulphuric acid, if it did not combine with the sulphuric acid. The contraction in volume when the sulphuric acid or water was added to the acetic acid was also taken into account in these corrections.

Doubtless the above assumption does not hold rigidly, and slight errors are the consequence, but it is fairly certain that their magnitude cannot be great. However, the main features in this combination of sulphuric acid with water appear so clearly from the results, that they would be entirely unmasked by the small errors to which reference is above made.

In the series of determinations given in Table VI the largest amount of water was used. The quantity of sulphuric acid added in the first determination was 0.109 gram. There were then present about thirty-eight equivalents of water to one of sulphuric acid. Yet from the column of "difference" it will be seen that the "difference" is very nearly twice the lowering produced by the sulphuric acid alone. This means that each molecule of the sulphuric acid has combined with two, and only two, molecules of water, which have disappeared, so far as the lowering of the freezing-point is concerned. The "difference" is slightly greater than twice the lowering produced by the sulphuric acid alone, but this is doubtless due to the fact that an equivalent of water produces a greater lowering of the freezing-point than an equivalent of sulphuric acid. This is seen from the gram-molecular lowerings of the two in Tables A and B. It is, however, impossible to say whether the molecule $H_2SO_4.2H_2O$ would give exactly the same lowering as the molecule H_2SO_4 or as the molecule H_2O.

As the quantity of sulphuric acid approaches one half-equivalent to the water, the "difference" becomes less than the lowering produced by two molecules of water to each of sulphuric acid. At one half-equivalent of sulphuric acid this "difference" is considerably less, showing that at this point some of the water remains uncombined, and some of the sulphuric acid has probably not formed a hydrate higher than $H_2SO_4.H_2O$. As the quantity of sulphuric acid is increased beyond one half-equivalent, more and more of the hydrate $H_2SO_4.H_2O$ seems to be formed, and when an equivalent of sulphuric acid is present the water is practically all combined with the acid, probably as this hydrate. The fact that when one half-equivalent of sulphuric acid is present a part of the water is not combined to form this hydrate $H_2SO_4.2H_2O$, is doubtless due to the action of the acetic acid, dissociating this compound. That the acetic acid can probably cause such dissociation will be seen later when we consider the more dilute solutions of the hydrates in the acid and when a smaller excess of water is present.

The same general facts brought out by the results in Table VI are also established by the results in Tables IV and V, where slightly smaller quantities of water were used.

In the series of determinations, the results of which are given in Tables III, II and I, the amounts of water used were very much

smaller, and the solutions of the hydrates in the acetic acid, when all the water was combined, were very much more dilute. Under these conditions some entirely new facts have appeared. Let us consider, *e. g.*, the second determination in Table III, and the "difference" is far less than would correspond to the hydrate $H_2SO_4.2H_2O$, yet more than four equivalents of water are present to one of sulphuric acid. The same fact is seen even more clearly in the first determination of Table II, where more than seven equivalents of water are present to one of sulphuric acid, and where the entire amount of water is small. Here the "difference" is less than it would be if each molecule of sulphuric acid were combined as $H_2SO_4.H_2O$. Under these conditions of dilution in the acetic acid there must be free sulphuric acid, and this in the presence of seven equivalents of water. Yet we have seen from the results in Table VI that when sulphuric acid and water are present in these proportions and in quantities sufficient to give a much more concentrated solution of the hydrates in the acetic acid, every molecule of the sulphuric acid is in combination with two molecules of water.

To test this question of the dissociation of the hydrates still further, a very small amount of water (0.068 gram) was added to the acetic acid and then small amounts of sulphuric acid added, and the freezing-points very carefully determined. The results of these measurements are given in Table I. In the first determination more than four equivalents of water are present, yet the "difference" shows that less than one-half of the sulphuric acid is in combination with even one molecule of water. In the fourth determination somewhat more than an equivalent of sulphuric acid is present, yet less than half of the water is combined. For this dilution it is only when the amount of sulphuric acid has somewhat exceeded two equivalents that all the water is combined, yet for the concentrations represented in Table VI all the water was combined when one equivalent of acid was present.

There was just a possibility that the explanation of the above results was not to be found in the dissociation of the hydrates of sulphuric acid, but in an electrolytic dissociation of the sulphuric acid itself in the acetic acid or in the acetic acid and water. It was improbable that any large amount of electrolytic dissociation should take place at these concentrations; yet to obtain light on this point the "conductivity" of the solutions must be determined.

The conductivity of the pure acetic acid was at first determined, then the conductivity of the acid to which small amounts of water had been added; also the conductivity of the acetic acid to which small amounts of sulphuric acid had been added, and finally the conductivity of the acetic-acid solutions containing both water and sulphuric acid.

The conductivity was calculated from the well-known formula

$$\mu = K\frac{v.a}{w.b}.$$

μ = molecular conductivity; K = the "capacity" of the vessel used; v = the volume of the solution in liters which contains a gram-molecular weight of the electrolyte; a = reading on the left side of the bridge; w = the resistance in ohms introduced into the circuit; b = reading on the right side of the bridge. The results of these determinations are given below.

Conductivity Results.

Conductivity of pure acetic acid, $\mu = 0.00001$.

Conductivity of acetic acid with small amounts of water:

Water added to 10 cc. CH_3COOH.	v.	μ.
0.071 gram	2.5	0.0002
0.287	0.65	0.0004

Conductivity of acetic acid with small amounts of sulphuric acid:

Sulphuric Acid added to 10 cc. CH_3COOH.	v.	μ.
0.121 gram	8.1	0.098
0.371	2.7	0.465
0.918	1.12	1.559
1.798	0.6	2.506
3.095	0.37	2.313
4.403	0.27	1.989
5.499	0.23	1.973

Conductivity of acetic acid to which small amounts of water and sulphuric acid have been added:

Series I.

Amount of Water added to 10 cc. CH_3COOH.	Amounts of Sulphuric Acid added to 10 cc. $CH_3COOH + H_2O$.	v.	μ.
0.071 gram	0.042 gram	23.35	0.331
	0.085	11.64	0.632
	0.198	5.05	0.687
	0.565	1.80	1.524
	1.175	0.88	2.256
	1.723	0.62	2.800

Series II.

Amount of Water added to 10 cc. CH_3COOH.	Amounts of Sulphuric Acid added to 10 cc. $CH_3COOH + H_2O$.	v.	μ.
0.287 gram	0.108 gram	9.34	2.219
	0.635	1.63	2.770
	1.712	0.64	2.888
	2.990	0.39	2.679
	4.367	0.28	2.347

The conductivity of the pure acetic acid was nearly zero, as would have been expected. The conductivity of acetic acid to which small amounts of water were added was also very slight. This agrees well with what is already known, since Ostwald[1] has shown that the dissociation of a tenth-normal solution of acetic acid in water is only about one per cent., and the same fact has been established by my own work on the lowering of the freezing-point.

The results show, however, that when sulphuric acid is added to the acetic acid there is a slight conductivity. It is probable that it is the sulphuric and not the acetic acid which is dissociated, for the dilution of the sulphuric acid in the acetic is much greater than that of the acetic in the sulphuric, and, for the same concentrations, sulphuric acid is much more readily dissociated in water than is acetic acid. The "volume," v, is calculated for the sulphuric acid in the acetic acid as a solvent. The "molecular conductivity," μ, increases with increase in concentration to a maximum and then diminishes slightly. Kablukoff[2] found that the "molecular con-

[1] Ztschr. phys. Chem. **3**, 174. [2] *Ibid.* **4**, 429.

ductivity" of hydrochloric acid in ether and isoamyl alcohol decreased with increase in the dilution of the solutions.

When both water and sulphuric acid were added to the acetic acid in quantities as small as are given above, the solutions show also a slight conductivity, but only a little greater than when the sulphuric acid was added alone. It seems, therefore, that the small amount of water present exerts but little effect on the electrolytic dissociation. Since this is true, the "volume" v was here also calculated for the sulphuric acid in the acetic acid.

It is at present impossible to calculate the exact amount of dissociation of these solutions in acetic acid from the known values of μv, because the value of $\mu\infty$ for sulphuric acid in acetic acid is unknown. This would probably involve a determination of the velocity of migration of the ions of sulphuric acid in acetic acid. But the very small values found for μv render it very probable that the electrolytic dissociation of the sulphuric acid under the above conditions is small, and far too small to account for the results obtained.

The only satisfactory explanation of the results, then, seems to be the one offered,—that the hydrates of sulphuric acid are unstable in very dilute solutions in acetic acid when the excess of water present is not very considerable. Under the same conditions an excess of sulphuric acid would probably have a similar effect in increasing the stability of these hydrates.

The Action of Water and Ethyl Alcohol on the Freezing-point of Acetic Acid.

The lowerings of the freezing-point of acetic acid produced by different amounts of alcohol alone were first determined and plotted as Curve 3. The ordinate-unit = 0.1°. and the abscissa-unit = 0.2°. The curve deviates only slightly from a straight line. With the exception of the first determination, the molecular lowering also changes only slightly.

The object in studying the action of the alcohol and water together on the lowering of the freezing-point of acetic acid, was to determine if any combination between the two took place. The results show that the lowering found is very nearly the sum of the lowerings produced by each separately in the presence of the other. The small "difference," which increases slightly with the

amount of alcohol, is possibly caused by the fact that the corrections introduced for changes in volume due to the addition of water and alcohol are not exact.

Lowering of the Freezing-point of Acetic Acid by Small Quantities of Ethyl Alcohol.

TABLE VII.

Wt. Alcohol added to 26.335 grams CH_3COOH.	Lowering of the Freezing-point.	Gr.-mol. Low. 46 grams C_2H_6O 1000 grams CH_3COOH.
0.087 gram	0.305°	4.25
0.261	0.850	3.95
0.443	1.450	3.96
0.617	2.000	3.91
0.791	2.510	3.84
0.976	3.038	3.77
1.168	3.565	3.70
1.343	4.059	3.66
1.518	4.555	3.63
1.696	5.045	3.60

Lowering of the Freezing-point of Acetic Acid by Ethyl Alcohol and Water.

TABLE VIII.

26.335 grams acetic acid. 0.245 gram water.

Amounts of C_2H_5OH.	Lowering by C_2H_5OH.	Lowering by H_2O.	Sum of the last two.	Lowering found.	Difference.
0.085 gram	0.305°	1.760°	2.065°	2.050°	0.015°
0.273	0.880	1.740	2.620	2.575	0.045
0.452	1.465	1.720	3.185	3.105	0.080
0.621	2.000	1.705	3.705	3.557	0.148
0.780	2.455	1.690	4.145	3.968	0.177
1.155	3.505	1.665	5.170	4.975	0.195

These determinations were the more desirable because Mendeléeff[1] has stated that the specific gravities of solutions of alcohol in water indicate the following compounds:

$$3C_2H_6O + H_2O,$$
$$C_2H_6O + 3H_2O,$$
$$C_2H_6O + 12H_2O.$$

[1] Ztschr. phys. Chem. **1**, 284.

My results furnish no evidence whatsoever in favor of the existence of such compounds. It may be said, of course, that such compounds are unstable in the acetic acid. Yet it seems probable that if there were any strong attraction between the water and the alcohol, it would manifest itself at least to some extent in the first determination, where some eight equivalents of water are present to one of alcohol, and where the total excess of water present is not inconsiderable.

Pickering[1] has also studied the action of the same compounds on the lowering of the freezing-point of acetic acid, and found that no combination between the two took place.

Action of Water and Dry Sodium Acetate on the Freezing-point of Acetic Acid.

The neutral acetate of sodium combines with three molecules of water, and many of the acid acetates also contain water. The following have been described by Vielliers:[2]

$$C_2H_3O_2Na.C_2H_4O_2,$$
$$C_2H_3O_2Na.2C_2H_4O_2.H_2O,$$
$$5C_2H_3O_2Na.4C_2H_4O_2.6H_2O,$$
$$4C_2H_3O_2Na.C_2H_4O_2.11H_2O,$$
$$5C_2H_3O_2Na.2C_2H_4O_2.13H_2O.$$

Which is formed depends, according to Vielliers, not simply on the relation between the amounts of acetate and acid, but also on the amount of water present. If the acetate which existed in the solution of acetic acid combined with water, this would be shown by the lowering of the freezing-point of the acetic acid. Sodium acetate was therefore carefully dried, and the lowering of the freezing-point produced by this alone determined. The results are plotted in Curve 4, in which the ordinate-unit = 0.1n. and the abscissa-unit = 0.2°. The molecular lowering increases slightly with the amount of acetate. This may be due to the disappearance of a small amount of acid forming the acid acetate. The results in Table X seem to show that a very small amount of water was combined with the salt. Those in Table XI show a much greater "difference," indicating the combination of more water, but even here the amount is far less than would correspond to one molecule of water for each molecule of the acetate.

[1] Ber. d. chem. Ges. **24**, 1584.

[2] Compt. rend. **84**, 774; **85**, 755.

Lowering of the Freezing-point of Pure Acetic Acid by Small Amounts of Sodium Acetate.

TABLE IX.

Wt. CH_3COONa added to 26.335 grams CH_3COOH.	Lowering of the Freezing-point.	Gr.-mol. Lowering 82 grams CH_3COONa 1000 grams CH_3COOH.
0.109 gram	0.210°	4.16
0.288	0.600	4.50
0.568	1.145	4.35
0.857	1.690	4.26
1.246	2.488	4.31
1.586	3.180	4.33
1.945	3.940	4.37

Lowering of the Freezing-point of Pure Acetic Acid by Sodium Acetate and Water.

TABLE X.

26.335 grams acetic acid. 0.606 gram sodium acetate.

Amounts of H_2O in grams.	Lowering by H_2O.	Lowering by CH_3COONa.	Sum of the last two.	Lowering found.	Difference.
0.145	1.080°	1.220°	2.300°	2.360°	−0.060°
0.279	2.010	1.205	3.215	3.180	+0.035
0.409	2.810	1.200	4.010	3.905	0.105
0.553	3.625	1.195	4.820	4.640	0.180

TABLE XI.

26.335 grams acetic acid. 1.645 grams sodium acetate.

Amounts of H_2O in grams.	Lowering by H_2O.	Lowering by CH_3COONa.	Sum of the last two.	Lowering found.	Difference.
0.085	0.645°	3.310°	3.955°	3.585°	0.370°
0.194	1.430	3.285	4.715	4.210	0.505
0.315	2.230	3.270	5.500	4.870	0.630

Conclusion.

The chief interest connected with the results obtained in this work seems to be in connection with the facts brought to light in reference to the hydrates of sulphuric acid. When the quantity of water in proportion to the acetic acid is as great as in Table VI, and an equivalent of sulphuric acid is added, the water is all

in combination, and probably as the hydrate $H_2SO_4.H_2O$. If under these conditions, say a tenth of an equivalent of sulphuric acid be added to the acetic acid and water, every molecule of sulphuric acid is in combination with two molecules of water as $H_2SO_4.2H_2O = S(OH)_6$, which is the normal hydrate. When as much as *thirty-seven* equivalents of water are present to one of sulphuric acid, there is no evidence of the formation of hydrates with more water than $S(OH)_6$. Evidence is furnished of the existence of the compounds $H_2SO_4.H_2O$ and $H_2SO_4.2H_2O$. The higher hydrates containing a much greater number of molecules of water to the sulphuric acid, which have been thought by Mendeléeff to be probable, find no support from my results. On the contrary, if such did exist one would expect to obtain some indication of their formation under some of the conditions which have been here employed.

When, however, much less water is present in proportion to the acetic acid, as in Table I, more than two equivalents of sulphuric acid must be present before all the water is in combination with the acid. If under these conditions, say a fifth of an equivalent of sulphuric acid be present, much of this remains free, and the remainder probably combined only as $H_2SO_4.H_2O$. These hydrates are somewhat unstable in the acetic acid when their solutions are very dilute, and when the excess of water present is not very great. They can be regarded as dissociated under these conditions by the acetic acid into sulphuric acid and water.

The hydrates of alcohol, which Mendeléeff supposed to have been indicated by the specific gravity of the solutions of alcohol in water, find no support from the results obtained in connection with this work.

In conclusion, I wish to express my sincere thanks to Dr. Svante Arrhenius, from whom valuable suggestions were received, and in whose well-equipped laboratory in Stockholm this piece of work was carried out.

PHYSICAL INSTITUTE, STOCKHOLM, *September*, 1893.

THE ATOMIC WEIGHT OF PALLADIUM.

By Edward H. Keiser and Mary B. Breed.

In an investigation by one of us, published in 1889,[1] upon the atomic weight of palladium, it was found that palladium diammonium chloride, $Pd(NH_3Cl)_2$, is a much more suitable compound for the determination of the atomic weight of this metal than the double chloride of palladium and potassium that had previously been used by Berzelius for this purpose. The palladammonium chloride is a compound that can be prepared in a state of great purity; it can be thoroughly dried without undergoing decomposition; it is not hygroscopic, and the amount of palladium in it can be accurately determined by heating it in a current of hydrogen, whereby ammonium chloride is volatilized and metallic palladium remains behind. As the result of nineteen determinations made in this way upon different preparations of the compound, the number 106.35 was obtained for the atomic weight. This number was calculated directly from the weights of the substances in air. If the weights be reduced to a vacuum, then the value of the atomic weight becomes 106.27. Recently several investigators have worked upon this subject and have published results, some of which are considerably higher and others decidedly lower than the number 106.3.

Thus Bayley and Lamb,[2] after examining a number of palladium compounds for the purpose of devising a new method of determining the atomic weight, have adopted the method described above, namely, reduction of palladammonium chloride in a current of hydrogen, and find as the mean of ten determinations the value 105.46. From a series of chlorine determinations in the compound they obtained the number 106.37, but this they regarded as less accurate than the other.

Keller and Smith[3] have also published the results of their determinations of the atomic weight of palladium. They too have determined the ratio of palladium to palladammonium chloride. Weighed quantities of the compound were dissolved in dilute ammonia, and the solution subjected to electrolysis in platinum dishes containing a deposit of metallic silver. The

[1] This Journal **11**, 398. [2] J. Chem. Soc. (1892) **61**, 745. [3] This Journal **14**, 423.

increase in weight of the dish was taken as the weight of the palladium deposited. Nine determinations were made, from which the number 106.91 was obtained for the atomic weight.

Joly and Leidié[1] have made some preliminary experiments on the atomic weight of palladium. Weighed quantities of the double chloride of potassium and palladium were dissolved in water, and the metal precipitated by electrolysis. From the ratio of palladium to potassium palladium chloride they obtain the number 105.44 for the atomic weight.

The different determinations, then, stand as follows:

Berzelius,	1829,	106.2.
Keiser,	1889,	106.3.
Bayley and Lamb,	1892,	105.5.
Keller and Smith,	1892,	106.9.
Joly and Leidié,	1893,	105.4.

As these recent determinations differ from one another by as much as one and a half units, it seemed desirable to take up the work again and to endeavor to establish this constant with a greater degree of certainty than has yet been attained. We have endeavored in the first place to find some compound of palladium that could be vaporized, and therefore subjected to fractional distillation. For, as Stas has shown, it is only the substances that can be vaporized that can be obtained in a high state of purity.

Distillation of Palladium Chloride in a Current of Chlorine.

We have found that palladium dichloride, $PdCl_2$, can be distilled at a low red heat in a current of chlorine. For the purpose of obtaining palladium chloride and purifying it by distillation, spongy palladium, obtained by the reduction of palladium diammonium chloride—the metal remaining from the atomic weight determinations of 1889—was placed in a thin layer in one end of a combustion-tube. In the middle of the tube there was a constriction which prevented liquid from flowing from one end to the other when the tube was in a horizontal position. The end of the tube containing the palladium was connected with an apparatus furnishing a stream of dry chlorine. The tube was placed in a combustion-furnace and so arranged that that portion of the tube

[1] Compt. rend. (1893) **116**, 146.

containing the palladium could be heated to a bright red heat. The chlorine was prepared from hydrochloric acid and manganese dioxide, and after washing with water was led through two bottles containing concentrated sulphuric acid. The gas after passing through the tube containing the palladium and before escaping into the air, was conducted through water contained in two wash-bottles to remove palladium chloride from it. After the chlorine had displaced all the air in the apparatus, that portion of the tube containing the palladium was heated in the furnace. When the temperature began to approach a low red heat the metal combined rapidly with the chlorine. Soon it began to glow, and in a few moments the entire quantity of metal had been converted into chloride. The heating was continued and a slow current of chlorine passed through the tube. The palladium chloride melted and became a dark liquid, and soon a red sublimate began to appear in the cold portion of the tube. The heating was continued, and after a time the entire cross-section of the tube for a length of several inches became filled with minute dark-red, needle-shaped crystals. The molten chloride in the front portion of the tube appeared to be boiling, as gas-bubbles were slowly evolved from it. After a considerable quantity of the crystalline sublimate had been prepared in this way the tube was allowed to cool and the crystals removed. An analysis showed that they were palladium dichloride, $PdCl_2$.

0.2011 gram gave on reduction in a current of hydrogen 0.0804 gram Cl.

	Calculated for $PdCl_2$.	Found.
Cl	40.01	39.98

When the crystals are heated in a stream of chlorine they melt and form when cold a dark-red crystalline mass consisting of dichloride mixed with monochloride. The crystals are deliquescent and absorb moisture in the air.

Several distillations of palladium chloride in a current of chlorine were now made, and a quantity of the distilled chloride weighing a little more than ten grams was obtained. This was redistilled in the same manner, and of the distillate the more volatile and the least volatile portions were rejected and only the middle portion used for the subsequent work.

We hoped at one time to use the dichloride directly for the determination of the ratio of palladium to chlorine, but owing to its

deliquescent nature and the fact that when melted the dichloride is partially converted into monochloride, we abandoned experiments in this direction and decided to convert the dichloride into palladium diammonium chloride. For this purpose the redistilled chloride was dissolved in distilled water to which a few drops of hydrochloric acid had been added. Ammonia was added gradually and the solution warmed upon the water-bath until the flesh-colored precipitate had dissolved. The filtered solution was diluted with a large volume of water, and into the dilute solution a current of pure hydrochloric acid gas was passed. The palladammonium chloride thus formed was washed repeatedly by decantation, and finally upon the filter. It was then dissolved in dilute ammonia and reprecipitated with hydrochloric acid gas, thoroughly washed and then dried in desiccators.

Analysis of the Palladium Diammonium Chloride.

The ratio of palladium to palladammonium chloride was determined by reducing weighed quantities of the dried compound in a current of hydrogen. The palladammonium chloride was weighed in platinum boats. It was dried in an air-bath at a temperature of 110°–120° until constant weight was obtained. The boat was then introduced into a combustion-tube through which a current of pure hydrogen was passed. The hydrogen was made by the action of pure dilute hydrochloric acid upon pure zinc, and was washed with alkaline lead solution and potassium permanganate. It was then dried by passing over solid caustic potash, after which it passed over red-hot metallic copper, and, finally, before entering the reduction-tube it was dried with phosphorus pentoxide. After the hydrogen had been passing through the reduction-tube for some minutes and all air had been expelled, the portion of the tube containing the boat was heated very gently. The palladammonium chloride unites with the hydrogen very gradually under these circumstances. There is no decrepitation whatsoever, and by gently raising the temperature the ammonium chloride slowly sublimes. The sublimate in all cases was found to be perfectly snow-white in appearance. *There was absolutely no loss of palladium by volatilization nor by decrepitation,*[1] as was

[1] Keller and Smith: This Journal **14**, 423, found that palladium was volatilized. This was no doubt due to a rapid reduction of the imperfectly dried compound in a strong current of hydrogen. The metal used by one of us (K.) in the earlier determinations was not, as they suppose, obtained from Eimer & Amend in New York.

shown by a careful examination of the aqueous and acid washings of the tube after the reduction had been finished. In neither solution could a trace of palladium be found when tested with potassium iodide or with hydrogen sulphide. It is only when an imperfectly dried specimen of palladammonium chloride is heated very rapidly in a current of hydrogen that there is loss by spattering and the mechanical carrying away of minute particles of palladium.

The results of the analysis of the palladammonium chloride prepared from distilled palladium chloride are as follows:

Number.	Weight of $PdN_2H_6Cl_2$ taken.	Weight of Pd obtained.	Atomic Weight.
1	1.60842	0.80997	106.271
2	2.08295	1.04920	106.325
3	2.02440	1.01975	106.334
4	2.54810	1.28360	106.342
5	1.75505	0.88410	106.341
Total,	10.01892	5.04662	[106.325]

Reducing now the weights in air to the weights in a vacuum, by adding the weight of air displaced, we obtain the ratio:

$$PdN_2H_6Cl_2 : Pd :: 10.02373 : 5.04717 \text{ or } Pd = 106.246.$$

In this calculation the specific gravity of palladium is taken as 11, and that of the palladium diammonium chloride as 2.5, values found as the result of duplicate determinations. The following atomic weights have been used: $H = 1$, $N = 14.01$, $Cl = 35.37$. The weight of a cubic centimeter of air is taken as 0.0012 gram.

Purification of Palladium in the Wet Way.

In order to test the accuracy of the determinations made in 1889, we decided to purify some palladium by the method then used, with additional precautions. A piece of palladium foil, weighing about fifteen grams, was therefore dissolved in *aqua regia*, and the solution of dichloride thus obtained evaporated to dryness. The residue was then dissolved in water, to which a little hydrochloric acid was added, and the filtered solution was treated with ammonia and warmed upon the water-bath until the precipitate first formed was dissolved. The insoluble residue,

containing iron and other impurities, was filtered off; but the filtrate was pale bluish-green in color, owing to the presence of copper. Hydrochloric acid gas, made by allowing pure concentrated sulphuric acid to act on pure, strong hydrochloric acid, and washed through a concentrated solution of hydrochloric acid, was passed into the solution. The palladium diammonium chloride thus precipitated was washed by decantation and then upon the filter with the aid of a suction-pump, and afterwards redissolved in very dilute ammonia. This process of precipitating and dissolving the substance was repeated five times. All rhodium and the last trace of iron were thus removed; the bluish color gradually disappeared from the ammoniacal solution, which became a clear straw color, showing that all copper had been removed. The salt was then dried in desiccators, and the metal obtained from it by reduction in hydrogen, as before described.

The spongy metal was then again dissolved in *aqua regia*, evaporated repeatedly with hydrochloric acid to expel nitric acid, and the chloride dissolved in very dilute hydrochloric acid. In order to make sure that no gold was present, sulphur dioxide was passed into the solution. The gas was prepared from pure sulphuric acid and copper, was washed through water, and run into the solution of palladium until the color changed from dark red to yellow. The solution was protected from dust and allowed to stand for a week, but no gold was found to be precipitated, and the solution was therefore evaporated to dryness to expel sulphur dioxide. The residue, after being dissolved in water containing hydrochloric acid, and treated with ammonia, was converted into palladammonium chloride in the same manner as before. At this point, however, it became evident that not only had the introduction of sulphur dioxide been unnecessary for the purification of the substance, but had become itself a source of difficulty; for the palladammonium chloride was now dull brownish yellow, instead of pure orange-yellow as before. Dissolving and reprecipitating did not alter the appearance of the salt, and when dried it turned dark brown on all the surfaces exposed to the air. We decided that it would be necessary to reduce to the metallic form in order to expel sulphur. This was done in the same way as before, and the reduced metal was again converted into palladammonium chloride. Though the freshly precipitated salt was now of the proper color, yet it changed as soon as it dried, becom-

ing dull lemon-yellow throughout, and turning brown on the exposed surfaces. That the source of difficulty lay in some foreign substance present in the salt itself was shown by the fact that the change in color took place when the most careful precautions were taken to exclude all laboratory fumes from the workroom, and when the salt was placed in the desiccator as soon as the washing was completed. After precipitating and redissolving the salt three times, but without removing the impurity, we reduced it again in a current of hydrogen, and then, placing the reduced metal in a hard-glass tube, through which hydrogen was passing, heated it in the combustion-furnace and kept the metal at a bright-red heat for five minutes. After cooling it was dissolved again in *aqua regia*, evaporated repeatedly with hydrochloric acid, dissolved in water and a few drops of the acid, and the solution was then treated with mercuric cyanide in slight excess. The palladium cyanide thus precipitated was allowed to settle, and was washed by decantation repeatedly. It was then washed on the filter, dried in desiccators, and reduced to metallic form by heating in the air. Cyanogen gas was given off, and after the reaction was complete, the heating was continued for about an hour, to expel any mercury that might have been retained mechanically by the very gelatinous precipitate of palladium cyanide. The metal, which was partly oxidized, was reduced in a Rose crucible in a current of hydrogen, dissolved in *aqua regia*, the solution evaporated repeatedly with hydrochloric acid and then digested with ammonia. Just as the precipitate thus formed was about all dissolved, a white crystalline precipitate separated in small quantity, which, when filtered off, proved to be the so-called "white precipitate" formed by the action of ammonia on mercuric chloride. The small quantity of mercury that could not be removed by heating was thus separated by filtration, and the palladium was then precipitated as palladammonium chloride by running in hydrochloric acid gas. The precipitate, after washing, was dissolved and reprecipitated, to prove that all mercury had been removed, washed and dried for several months in a desiccator over solid caustic potash.

Analysis of Palladium Diammonium Chloride purified by Precipitation.

The palladium in the salt was determined in the same way as in that purified by distillation—*i. e.*, the substance was weighed

out in platinum boats, dried to constant temperature, and reduced in a current of hydrogen prepared and purified in the manner before described. In these analyses, as in the others, the sublimate was in every case tested for palladium which might have been carried out of the boat, but no trace of the metal was found in the washings.

The results of the analyses of the palladium diammonium chloride prepared in the wet way are as follows:

No.	Wt. of $Pd(NH_3Cl)_2$ taken.	Wt. of Pd found.	Atomic Weight.
1	1.50275	0.75685	106.297
2	1.23672	0.62286	106.296
3	1.34470	0.67739	106.343
4	1.49059	0.75095	106.353
Total,	5.57476	2.80805	[106.322]

Highest = 106.353
Lowest = 106.296
Difference = 0.057

Reducing the weights in air to the weights in vacuum by adding the weight of air displaced, we obtain the ratio:

$$PdN_2H_6Cl_2 : Pd :: 5.577436 : 2.808356,$$
or atomic weight of Pd = 106.245.

The value found is practically the same as in the first series.

The earlier determinations of one of us have been criticized on the grounds that sufficient precautions were not taken to ensure the purity of the palladammonium chloride that was analyzed, and that in the reduction of this compound in a stream of hydrogen there was loss by decrepitation and the mechanical carrying away of metal by the hydrogen. In repeating the work we have met these objections by devising a new method for the purification of palladium compounds, namely, the fractional distillation of palladium chloride in a current of chlorine. We have purified palladium chloride in this way and converted it into palladammonium chloride. We have also prepared the latter compound by the best known methods in the wet way. We have analyzed both specimens by reduction in pure hydrogen. We have shown that

this was done without loss of metal. And as the result we get in each case for the atomic weight the value **106.25**—a number that agrees very closely with the value first obtained, *viz.*, 106.27. We propose to continue the investigation and shall endeavor to determine this constant in other ways.

CHEMICAL LABORATORY, BRYN MAWR COLLEGE, *October*, 1893.

Contributions from the Chemical Laboratory of Harvard College.

LXXXI.—ON THE ACTION OF WATER UPON TRIBROMTRINITROBENZOL AND TRIBROMDINITROBENZOL.[1]

BY C. LORING JACKSON AND W. H. WARREN.

In an article[2] recently published, C. A. Lobry de Bruyn describes the action of an aqueous solution of sodic carbonate upon the unsymmetrical trinitrobenzol (1, 2, 4) which produces the dinitrophenol (OH, 1, 2, 4) by the replacement of a nitro group by hydroxyl. After we had shown in an earlier paper[3] that the nitro groups can be removed from tribromtrinitrobenzol by sodic alcoholates, M. Lobry de Bruyn suggested to us in the most courteous way that it would be interesting to see whether an aqueous solution of sodic carbonate would not have a similar effect on this substance, which seemed not improbable after his work already cited. The following paper contains an account of the work we undertook in accordance with this suggestion, the results of which can be briefly summarized as follows: Symmetrical tribromtrinitrobenzol (melting-point 285°) is converted by boiling with sodic carbonate and water into a mixture of the sodium salts of trinitrophloroglucin and a tribromdinitrophenol, $C_6Br_3(NO_2)_2OH$, melting at 194°, which, so far as we can find, has not been described as yet. Tribromdinitrobenzol (melting-point 192°; made from symmetrical

[1] The work described in this paper formed part of a thesis presented to the Faculty of Arts and Sciences of Harvard University for the degree of Doctor of Philosophy, by W. H. Warren.

[2] Recueil trav. chim. **9**, 185.

[3] Proc. Am. Acad. **25**, 164; This Journal **14**, 364.

tribrombenzol) gave under the same conditions a dibromdinitrophenol which melts at 147°–148°, a melting-point almost identical with that (146°–146.5°) of the only other dibromdinitrophenol known, recently made by Garzino[1] by the action of nitric acid on the propionic ester of metabromphenol. This coincidence is, however, purely accidental, as in Garzino's phenol the bromine atoms stand in the ortho and para, in ours in the meta positions, to the hydroxyl. As was to be expected, the two phenols gave different salts, the potassium salt made by Garzino containing one-half of a molecule of water, while ours is anhydrous; his barium salt containing three, ours two molecules of water. Mixed with the dibromdinitrophenol is an oily phenol, which we have not succeeded in purifying in spite of many attempts.

The two substances, therefore, act with water and sodic carbonate in the same general manner as with sodic ethylate, the trinitro compound in both cases showing two parallel reactions, in one of which nitro groups, in the other bromine atoms, are removed, while the dinitro compound in both cases loses part of its bromine. It is to be observed, however, that while the alcoholate removes two nitro groups from the trinitro, and two bromine atoms from the dinitro compound, water in each of these cases removes only one; although, like the alcoholates, it removes all three of the bromine atoms from the tribromtrinitrobenzol.

The constitution of the new tribromdinitrophenol can be only $C_6(OH)BrNO_2BrNO_2Br$, as the substance from which it is derived is symmetrical. The dibromdinitrophenol, on the other hand, can be either $C_6(OH)NO_2BrNO_2BrH$ or $C_6(OH)NO_2BrHBrNO_2$, and we have no experimental data for determining which of these two formulas is correct.

Action of Water and Sodic Carbonate on Tribromtrinitrobenzol.

As this action takes place very slowly it is better to carry it on as follows: Four or more flasks provided with return-condensers were charged each with about 1 gram of tribromtrinitrobenzol and a moderate quantity of a dilute solution of sodic carbonate, and allowed to boil for twelve or more hours. After a short time the solution turned yellow, and at the end of the boiling had become deep red. The unaltered tribromtrinitrobenzol was filtered out,

[1] Att. R. Acc. Sc. Torino **25**, 263; Ber. d. chem. Ges. **25**, R. 219.

and boiled again with a fresh solution of sodic carbonate. The deep-red filtrate showed the presence of sodic bromide and sodic nitrite when the proper tests were applied. When acidified with dilute sulphuric acid it turned from red to yellow, and a white precipitate was thrown down, to which we first turned our attention.

The white product of the reaction, which is insoluble in water, was purified by dissolving it in ammonic hydrate, precipitating the barium salt from this solution by means of baric chloride, and treating the precipitate with alcohol, in which the barium salt of this substance is soluble. The filtered alcoholic solution was evaporated to dryness, the residue recrystallized several times from hot water, and then converted back into the free phenol by treatment with dilute hydrochloric acid. The free phenol was next dissolved in as little hot alcohol as possible, diluted with water till a precipitate began to form, which was then redissolved by the addition of a drop or two of alcohol, when, upon cooling, the substance separated in good crystals. This rather long method of purification can be replaced by simple crystallization of the free phenol from alcohol and water in the way just described, but if an absolutely pure product is needed, the whole method described above should be used. After it showed the constant melting-point 194°, it was dried at 100° and analyzed with the following results:

I. 0.1951 gram substance gave 12 cc. N at 23° and 768.1 mm.

II. 0.2089 gram substance gave 0.2787 gram AgBr (Carius).

	Calculated for $C_6Br_2(NO_2)_2OH$.	Found. I.	II.
Nitrogen	6.65	7.00	...
Bromine	57.01	...	56.76

These analyses show that the substance is a tribromdinitrophenol, and as it must have been formed from the tribromtrinitrobenzol by replacing one of the nitro groups by hydroxyl, its constitution must be represented by the formula $C_6(OH)BrNO_2BrNO_2Br$. It is, so far as we are aware, the first tribromdinitrophenol that has been made.

To confirm the results of the preceding analyses the sodium salt was made by treating an excess of the phenol with pure sodic

hydrate, filtering, and crystallizing from hot water, when it separated in long filiform yellow needles.

0.3076 gram sodium salt gave 0.0504 gram Na_2SO_4.

	Calculated for $C_6Br_3(NO_2)_2ONa$.	Found.
Sodium	5.19	5.31

The sodium salt is soluble in ethyl or methyl alcohol even in the cold, and crystallizes from its alcoholic solution in long, flat, pointed needles.

Properties of Tribromdinitrophenol.—This substance crystallizes from dilute alcohol in square-ended needles usually grouped in arborescent or fan-shaped clusters looking like certain seaweeds; its color is white with a very faint shade of yellow. It melts at 194°, and is freely soluble in cold ethyl or methyl alcohol, or in ether, acetone, or glacial acetic acid; somewhat less soluble in benzol or chloroform, although still freely soluble in these liquids; soluble in carbonic disulphide; slightly in ligroïn; very slightly in cold water, somewhat more soluble in hot. Dilute alcohol is the best solvent for obtaining crystals. Its alcoholic solution is distinctly yellow. The three strong acids have no apparent action on it. With alkalies it forms colored salts. A solution of the sodium salt gave precipitates consisting of yellow needles with salts of zinc, nickel, manganese, cobalt, chromium, cadmium, or lead. Cupric salts gave light green needles. In order to characterize the substance still further, its barium salt was prepared and analyzed.

Baric Tribromdinitrophenylate, $[C_6Br_3(NO_2)_2O]_2Ba$.—This substance was made by adding baric chloride to a concentrated solution of the ammonium or sodium salt, collecting the precipitate, and recrystallizing it several times from hot water. The salt contained no water of crystallization.

I. 0.6621 gram salt gave 0.1545 gram $BaSO_4$.

II. 0.5066 gram salt gave 0.1182 gram $BaSO_4$.

	Calculated for $[C_6Br_3(NO_2)_2O]_2Ba$.	Found. I.	Found. II.
Barium	14.03	13.72	13.72

The baric tribromdinitrophenylate crystallizes from hot water in long yellow needles arranged in radiating circular groups. It is slightly soluble in cold water, more soluble in hot; freely in cold ethyl or methyl alcohol.

After the tribromdinitrophenol obtained by the acidification of the products of the reaction of water and sodic carbonate on tribromtrinitrobenzol, had been filtered out, the filtrate was extracted with ether to obtain the organic substance, whose presence was indicated by its yellow color. The extract thus obtained melted above 190°, and contained bromine, indicating the probable presence of some tribromdinitrophenol. Upon boiling it with an aqueous solution of potassic carbonate, and allowing the solution to cool, small orange needles were obtained, which on acidification yielded the tribromdinitrophenol, recognized by its crystalline form and melting-point. The highly colored filtrate from these crystals was now treated with dilute sulphuric acid, extracted with ether, and the extract crystallized from water by slow evaporation, when the characteristic hexagonal prisms of trinitrophloroglucin were obtained. As they showed a somewhat low melting-point, 163°–164°, instead of 167°,[1] the original substance and its barium salt were analyzed with the following results:

0.2130 gram substance gave 30.3 cc. N at 19.5° and 776.1 mm.

	Calculated for $C_6(OH)_3(NO_2)_3$.	Found.
Nitrogen	16.09	16.67

0.7080 gram barium salt gave 0.5409 gram $BaSO_4$.

	Calculated for $[C_6O_3(NO_2)_2]_2Ba_3$.	Found.
Barium	44.33	44.91

The barium salt contained no water of crystallization. These analyses leave no doubt that the substance is trinitrophloroglucin, and the behavior of tribromtrinitrobenzol with water is therefore represented by the following reactions:

$$C_6Br_3(NO_2)_3 + 3H_2O = C_6(OH)_3(NO_2)_3 + 3HBr.$$
$$C_6Br_3(NO_2)_3 + H_2O = C_6Br_2(NO_2)_2OH + HNO_2.$$

The action of sodic hydrate and water upon tribromtrinitrobenzol was similar to that of sodic carbonate and water, the products being trinitrophloroglucin and tribromdinitrophenol. The action in this case takes place somewhat more quickly than with the carbonate, but we preferred to use sodic carbonate in order to avoid the action of the boiling hydrate upon the glass of the flask.

[1] This Journal **15**, 609.

In the cold, sodic hydrate seemed to have no action on tribromtrinitrobenzol, which surprised us because Lobry de Bruyn[1] has found that it acts in the cold on the unsymmetrical trinitrobenzol.

Action of Tribromdinitrobenzol with Water and Sodic Carbonate.

Tribromdinitrobenzol (melting-point 192°; made from symmetrical tribrombenzol) was boiled with an aqueous solution of sodic carbonate in the way just described for the trinitro compound. The action in this case was so slow that it was found better to continue the boiling for at least twenty-four hours before filtering. As in the preceding case, the solution gradually became yellow, and later changed to red. After filtering out the unaltered tribromdinitrobenzol, the red filtrate, which contained sodic bromide and sodic nitrite, was acidified with dilute sulphuric acid, which turned it light yellow, and produced a cloudy precipitate, which after a long time collected on the bottom in the form of oil-drops. These were removed, the clear liquid extracted with ether, and the extract, which was small in amount and oily, added to the oil which had separated. This was then dissolved in ammonic hydrate and treated with baric chloride, when a precipitate was formed in a dark-red solution.

The insoluble barium salt was decomposed with hydrochloric acid, and the phenol thus set free crystallized from dilute alcohol until it showed the constant melting-point 147°–148°, when it was dried at 100°, and analyzed with the following results:

I. 0.1626 gram substance gave 0.1804 gram AgBr (Carius).

II. 0.2053 gram substance gave 15.7 cc. N at 26° and 759.9 mm.

	Calculated for $C_6HBr_2OH(NO_2)_2$.	Found. I.	II.
Bromine	46.78	47.22	...
Nitrogen	8.19	...	8.49

These results prove that the substance is a dibromdinitrophenol formed by the replacement of one atom of bromine by the hydroxyl group, and as it is made from a symmetrical tribrom compound it must be isomeric with the one melting at 140°–146.5° made by Garzino from metadibromphenol.

Properties of Dibromdinitrophenol.—This substance crystallizes from a hot alcoholic solution diluted with water until the substance

[1] Rec. trav. chim. **9**, 193.

begins to precipitate, in thick yellow needles with square ends, arranged in radiating groups, although occasionally forms with two comb-edges were observed. If crystallized from alcohol alone, in addition to the thick needles or prisms, other rather broad prismatic forms are observed, which have a notch in each end so that they resemble reels, or, when this formation is carried farther so that the notch has a flat bottom, crystals resembling spools are produced. Both these latter forms are very characteristic. It melts at 147°–148°; and is very freely soluble in ethyl or methyl alcohol even in the cold, in ether, acetone, or glacial acetic acid; freely soluble in benzol or chloroform; soluble in carbonic disulphide; nearly insoluble in ligroïn; water dissolves it to a certain extent when cold, still more, although not freely, when hot. The three strong acids have no apparent action on it. Alkalies form yellow salts with it.

Potassic Dibromdinitrophenylate, $C_6HBr_2OK(NO_2)_2$.—This salt was prepared by heating the free phenol with an aqueous solution of potassic carbonate, and was purified by crystallization from hot water. The salt was found to be free from water of crystallization. 0.1806 gram of the air-dried salt lost only 0.0005 gram at 120°. Garzino found one-half of one molecule of water in his potassic dibromdinitrophenylate. The salt dried at 120° gave the following result on analysis:

0.1664 gram salt gave 0.0390 gram K_2SO_4.

	Calculated for $C_6HBr_2OK(NO_2)_2$.	Found.
Potassium	10.29	10.52

The salt crystallizes from hot water in arborescent clusters of orange-yellow needles, which are somewhat soluble in alcohol, but not freely even when it is hot.

Baric Dibromdinitrophenylate, $[C_6HBr_2O(NO_2)_2]_2Ba.2H_2O$.—The salt was made by boiling the phenol with water and baric carbonate, and purified by crystallization from boiling water, when it was analyzed with the following results:

I. 0.2834 gram salt dried in the air lost 0.0116 gram at 120°.

II. 0.2834 gram air-dried salt lost 0.0135 gram at 120°.

III. 0.2831 gram air-dried salt lost 0.0121 gram at 120°.

	Calculated for $[C_6HBr_2O(NO_2)_2]_2Ba.2H_2O$.	Found. I.	II.	III.
Water	4.21	4.09	4.76	4.27

Three molecules of water of crystallization, the amount found by Garzino in his barium salt, would give 6.19 per cent. of water.

IV. 0.3923 gram salt dried at 120° gave 0.1112 gram $BaSO_4$.

V. 0.2668 gram salt dried at 120° gave 0.0754 gram $BaSO_4$.

	Calculated for $[C_6HBr_2O(NO_2)_2]_2Ba$.	Found. IV.	V.
Barium	16.73	16.66	16.62

The salt is yellow while it contains its water of crystallization, but turns orange as it loses it, and this change takes place in a desiccator over sulphuric acid, as under these circumstances it loses all but an insignificant fraction of the water that it contains. The dried salt absorbs water very eagerly from the air, turning from orange to yellow again. It crystallizes from boiling water in clusters of radiating needles, and is soluble in alcohol.

The dark-red filtrate from the precipitate of the barium salt of dibromdinitrophenol gave, upon acidification, an oily precipitate, which has resisted all our efforts to bring it into a state fit for analysis; it is probable that this could be done by often-repeated fractional precipitation, but we do not think the identification of the substance of sufficient importance to justify the large expenditure of time and work necessary to provide material enough for this purpose. Several analyses, which we made to determine the purity of our preparations, seemed to point to the presence of a substance having the composition $C_6HBr_2NO_3(OH)_2$, but, as at the same time they proved that our products were decidedly impure, no weight should be given to this indication, although the formation of some such substance is to be expected from the appearance of sodic nitrite among the products of the reaction.

Sodic hydrate acts upon tribromdinitrobenzol in the same way that sodic carbonate does, but somewhat more rapidly. It has apparently no action in the cold.

LXXXII.—TRIANILIDODINITROBENZOL AND CERTAIN RELATED COMPOUNDS.

By C. Loring Jackson and H. N. Herman.

In a paper[1] published last year by one of us and W. B. Bentley, two forms of anilidotrinitrophenyltartronic ester were described,

[1] Proc. Am. Acad. **26**, 67; This Journal **14**, 348.

one of which was red and melted at 143°, the other yellow with a melting-point of 122°. We have undertaken a more complete study of this subject because the existence of these two modifications, if they are really chemical isomers, is not explained by any of the present theories of isomerism, unless indeed this should prove to be a case of an unsymmetrical nitrogen atom according to the hypothesis proposed by Hantzsch and Werner.[1] The anilidotrinitrophenyltartronic ester can be prepared in quantity only at a great expense of time and labor. It seemed wise, therefore, to begin our work by an examination of some related substances for similar modifications, as, if such were discovered in the case of a more accessible compound, their complete characterization could be worked out with greater ease. Unfortunately, as the new modifications obtained during these experiments were not so well marked as those already found, they could not be used to advantage for this purpose, and this work has taken so much time that the fuller study of the two forms of anilidotrinitrophenyltartronic ester could not be entered upon before the departure of one of us from Cambridge. The work contained in this paper, therefore, relates principally to the trianilidodinitrobenzol, which we have found appears both in red and yellow crystals, differing most strikingly in color and habit, but melting apparently at the same temperature, and passing from one form to the other with great ease, so that it is doubtful whether they should be considered true isomers. Nevertheless, it has seemed to us that, in the present state of our knowledge of isomers, a description of such closely related modifications as these might be of advantage to the science, and we therefore publish our results, which we think the more interesting because the triparatoluidodinitrobenzol shows an exactly similar behavior. On the other hand, we have not succeeded as yet in obtaining such forms from the triorthotoluidodinitrobenzol, although it is possible that they may exist, but that the second modification is less stable than those of the anilido and paratoluido compounds.

In searching for isomeric forms of the trianilidodinitrobenzol, which we have done by a great number of varied experiments, we discovered a compound of this substance with chloroform having the formula $C_6H(C_6H_5NH)_3(NO_2)_2.CHCl_3$, which crystallized in blackish-red, well-formed prisms, but lost its chloroform partially

[1] Ber. d. chem. Ges. **23**, 11.

even at ordinary temperatures. A similar addition-product was obtained with the corresponding para- but not with the ortho-toluido compound; an attempt will be made in this laboratory to trace the limits of this reaction.

Numerous attempts to prepare a second modification of trianilidotrinitrobenzol or of anilidotrinitrophenylmalonic ester have without exception led to negative results, as no change in the full yellow color or the crystalline form of either of these substances could be observed; but this result seems so strange in view of the occurrence of two modifications of the trianilidodinitrobenzol on the one hand, and of the anilidotrinitrophenyltartronic ester on the other, that a more careful study of these substances will be made hereafter, and the work extended to other substances, in the hope of collecting in time enough observations to determine the cause of the isomerism of the substituted tartronic ester.

Experiments with Trianilidodinitrobenzol.

In searching for isomeric forms of the trianilidodinitrobenzol we studied more carefully than before the crystallization of the substance from various solvents, and found that, when a mixture of benzol and alcohol was used as the solvent, it appeared in crystals of two sorts: one, the nearly square prisms of an orange color like that of potassic dichromate already described; the other, as yellow as potassic chromate, in bladed crystals, or plates looking like flattened monoclinic prisms terminated by two planes, or less commonly with square ends, which, when the cooling took place rapidly, appeared in circular groups of little needles. These two modifications differed entirely in crystalline habit and color, and resembled strongly the yellow and red forms of anilidotrinitrophenyltartronic ester, the discovery of which had led us to undertake this work; but whereas the two esters showed a difference of 21° in their melting-points (red 143°, yellow 122°), the yellow and red forms of the trianilidodinitrobenzol melted at the same temperature, 179°. To be sure, the yellow form turned red at about 140°, but there were no signs of melting, and we do not feel that such a change from yellow to orange-red is definite enough to have much significance. The yellow form was also much less stable than the corresponding form of the anilidotrinitrophenyltartronic ester, so that we have not obtained it absolutely free from the

orange modification. The best way for preparing it that we found was to crystallize the orange form from a mixture of benzol and alcohol containing much benzol, when a portion of the substance usually appeared in the yellow form. On the other hand, a single crystallization of the yellow crystals from a mixture of benzol and alcohol containing but little benzol, was sufficient to convert them completely into the orange prisms. As it was possible that the yellow crystals might be a compound containing alcohol or benzol of crystallization, instead of an isomer, we heated to 100° 0.3190 gram of the best we could obtain, which had been air-dried, but found that the loss was only 0.0004 gram, showing that this is not the explanation of the occurrence of this form.

The presence of a small amount of impurity seemed to be favorable to the existence of the modification crystallizing in plates, as, if a little tribromdinitrobenzol was present, crystals were obtained of this form, although usually a little more orange in color than that made from pure material, and these would undergo several crystallizations before they were converted into the orange form. A sample, which we obtained accidentally, was even more stable, and owed this stability to an oily impurity, the presence of which was indicated by the low melting-point, and which we finally succeeded in separating, but only after a great number of crystallizations, when the substance passed into the orange form; the amount of this impurity, however, was very small, as shown by the following analyses:

I. 0.2522 gram substance gave on combustion 0.6004 gram CO_2 and 0.1086 gram H_2O.

II. 0.2197 gram substance gave 31.6 cc. N at 25° and 755.4 mm.

	Calculated for $C_6H(C_4H_3NH)_3(NO_2)_3$.	Found. I.	Found. II.
Carbon	65.31	64.94	...
Hydrogen	4.30	4.79	...
Nitrogen	15.88	...	15.95

The substance gave no test for bromine with a copper wire, nor even when treated according to the method of Carius. As the amount of impurity is so small that we thought it could have no effect, we have used this preparation for the determination of the molecular weight of the yellow modification, which, with that of the orange prisms, was made by the method of Raoult, using benzol as the solvent, since preliminary experiments had shown

that these compounds were not sufficiently soluble in glacial acetic acid.

Yellow Plates.

Substance, 0.2290 gram; benzol, 10.299 grams; depression, 0.27°.

Orange Prisms.

Substance, 0.2561 gram; benzol, 10.468 grams; depression, 0.29°.

From these results the following molecular weights are obtained:

	Molecular Weight.
Yellow Plates	404
Orange Prisms	413
Calculated for $C_6H(C_6H_5NH)_3(NO_2)_3$	441

There can be no doubt, therefore, that the substances are not polymeric. The benzol-solutions obtained in the determinations were mixed with a little alcohol, and allowed to evaporate spontaneously (the substance is deposited as a varnish from benzol alone), when each yielded as the principal product the modification which had been originally dissolved in it, although in each case this was mixed with an insignificant amount of the other form.

From the observations given above we should infer that these two modifications of the trianilidodinitrobenzol are not true chemical isomers, but physical isomers, or perhaps rather that the substance is dimorphous.

We have made a great many experiments to get other isomeric forms of the trianilidodinitrobenzol, both by varying the method of preparation in every way we could devise, and by treating the orange prisms with reagents, which usually convert one stereoisomeric form into another, but have met with no forms except the two already described.

Compound of Trianilidodinitrobenzol and Chloroform.

If in crystallizing the trianilidodinitrobenzol a mixture of chloroform and alcohol was used instead of benzol and alcohol, dark red well-formed short prisms were obtained entirely different from

either of the forms just described. The whole of the substance could be converted into these prisms, if the solution in chloroform and a little alcohol was allowed to evaporate at temperatures from 50° to 70°. This substance, however, proved to be, not an isomer, but a compound with chloroform, since on heating some of the dry crystals with sodic hydrate and aniline a strong odor of phenyl isocyanide was perceived.

Our first attempts to analyze it showed that the chloroform was given up partially at ordinary temperatures, but that to drive off the remainder it was necessary to heat to 100°. Accordingly we proceeded as follows. A quantity of the orange trianilidodinitrobenzol melting at 179°, was dissolved in warm chloroform, and after the addition of a little alcohol poured into a large watch-glass to crystallize; when nearly all the chloroform had evaporated, the crystals were pressed as quickly as possible between filter-papers till free from adhering chloroform, and then transferred at once to a stoppered glass tube, in which they were weighed.

I. 1.5012 grams compound lost at 100° 0.3226 gram $CHCl_3$.

II. 1.4455 grams substance lost at 100° 0.3059 gram $CHCl_3$.

	Calculated for $C_6H(C_6H_5NH)_3(NO_2)_3.CHCl_3$.	Found. I.	II.
Chloroform	21.32	21.49	21.16

The residue was trianilidodinitrobenzol melting at 179°.

Properties of the Addition-compound of Trianilidodinitrobenzol and Chloroform.—This substance crystallizes in short thick prisms with both terminations well developed, apparently of the monoclinic system, which have a very dark brownish-red color not unlike that of well-crystallized potassic ferricyanide, and show a blue reflex. The chloroform is not securely held, part of it being given up even at ordinary temperatures with great rapidity, whereas heating to 100° is necessary to drive out the last traces. On this account its presence has only a slight effect on the melting-point, lowering it by a variable amount not exceeding 3° or 4°. Standing with alcohol if the crystals are small, or grinding them with it if they are large, also drives out the chloroform, leaving the usual orange prismatic form, and the same effect is produced by one crystallization from alcohol. Its action with other solvents was not studied.

Triparatoluidodinitrobenzol, $C_6H(C_7H_7NH)_3(NO_2)_3$.—10 grams of tribromdinitrobenzol were heated with 18 grams of paratoluidine

on the steam-bath for 18 or more hours; the reddish-black product was freed from the excess of toluidine by standing with dilute hydrochloric acid, followed by careful washing with hot water, and then purified by crystallization from benzol and chloroform. The substance thus obtained was not, however, triparatoluidodinitrobenzol, but its addition-compound with chloroform, as was shown by the isocyanide reaction, and the following analysis of the crystals dried by pressing between filter-papers.

0.9079 gram substance lost at 100° 0.1798 gram $CHCl_3$.

	Calculated for $C_6H(C_7H_7NH)_3(NO_2)_2.CHCl_3$.	Found.
Chloroform	19.83	19.81

Properties of Addition-compound $C_6H(C_7H_7NH)_3(NO_2)_2.CHCl_3$. —This substance crystallizes in long plates terminated at each end by two planes at a rather sharp angle to each other. It has a dark brownish-red color and loses part of its chloroform even at ordinary temperatures, but does not seem to be decomposed by alcohol so easily as the corresponding anilido compound.

In order to obtain the triparatoluidodinitrobenzol the preceding compound was dried at 100° until all the chloroform had passed off, and then crystallized from alcohol with a little benzol until it showed the constant melting-point 197°, when it was analyzed with the following results:

I. 0.1907 gram substance gave on combustion 0.4707 gram CO_2 and 0.1039 gram H_2O.

II. 0.2580 gram substance gave on combustion 0.6351 gram CO_2 and 0.1299 gram H_2O.

	Calculated for $C_6H(C_7H_7NH)_3(NO_2)_2$.	Found. I.	Found. II.
Carbon	67.09	67.30	67.14
Hydrogen	5.18	6.04	5.59

Properties of Triparatoluidodinitrobenzol.—This substance crystallizes from a mixture of benzol and alcohol in characteristic acute rhombic plates of a very dark purplish-red color somewhat like that of well-crystallized potassic ferricyanide, but redder and more purple. It melts at 197°, and is nearly insoluble in ethyl or methyl alcohol; freely soluble in benzol or chloroform; sparingly soluble in acetone or hot glacial acetic acid, almost insoluble in the latter solvent when cold.

If the dark brownish-red plates of triparatoluidodinitrobenzol are boiled with alcohol, the alcoholic extract deposits on cooling thread-like felted crystals of a yellow color, which change to red in the neighborhood of 180°, and melt at 197° like the original rhombic plates. We have found it impossible, however, to convert the whole of these plates into the yellow felted needles by this process. To prove that the yellow crystals did not contain alcohol of crystallization a portion of the preparation was heated at 120° until constant, when it was found that the loss was not more than would be mechanically retained by such a very spongy substance. The dried substance was then analyzed with the following result:

0.2096 gram substance gave 26.9 cc. N at 27.5° and 758.6 mm.

	Calculated for $C_6H(C_7H_7NH)_3(NO_2)_3$.	Found.
Nitrogen	14.49	14.10

We should add that 0.3991 gram of the dark-red plates air-dried when heated to 100° for four hours, lost only 0.0004 gram; so that this substance also is free from alcohol or benzol of crystallization. These observations show that the triparatoluido compound appears in two forms similar to those discovered with the anilido compound. Some other solvents besides alcohol convert the red form partially into the yellow, notably ether and acetone.

Triorthotoluidodinitrobenzol, $C_6H(C_7H_7NH)_3(NO_2)_3$.

This substance was most conveniently prepared by adding 12 grams of tribromdinitrobenzol to 35 grams of boiling orthotoluidine, stirring the mixture, and allowing it to cool as quickly as possible to avoid the formation of purple dye-stuff. The product was treated with dilute hydrochloric acid twice, the mixture allowed to stand for some time, and then washed thoroughly with water, after which it was purified by crystallization from benzol and alcohol, or chloroform and alcohol, until it showed the constant melting-point 243°, when it was analyzed with the following result:

0.2691 gram substance gave 34 cc. N at 23° and 763.3 mm.

	Calculated for $C_6H(C_7H_7NH)_3(NO_2)_3$.	Found.
Nitrogen	14.49	14.31

Properties.—The substance crystallizes in rather stout pointed needles of a full red color, which melt at 243°, and are somewhat

soluble in hot ethyl or methyl alcohol, less soluble in either cold; freely soluble in chloroform, acetone, or hot benzol, not very soluble in cold benzol; slightly soluble in hot ligroïn. Sodic hydrate had no apparent action on it. An attempt to make a chloroform-compound from it led to no result, the substance crystallized from chloroform showing no loss when heated to 120°. Nor have we succeeded in finding a yellow modification, although we have tried the methods which yielded such modifications with the corresponding compounds of aniline and paratoluidine; we think further experiments of this sort necessary, however, before we can be certain that such a modification does not exist. The high melting-point and the observations just mentioned indicate that this ortho compound is decidedly different from the corresponding para compound.

THE POLYMERIC MODIFICATIONS OF ACETIC ALDEHYDE, PARALDEHYDE AND METALDEHYDE.

By W. R. Orndorff and John White.

Historical.

The polymeric modifications of acetic aldehyde, paraldehyde and metaldehyde, have been the subject of many investigations, but the exact relation existing between them and the simple aldehyde from which they are derived is not clearly understood even at the present time.

The older treatises on the polymeric varieties of acetic aldehyde mention five modifications: (1) a fluid modification, boiling at 81° C., which Liebig[1] obtained by accident; (2) elaldehyde, melting at + 2° and boiling at 94°, obtained by Fehling[2] from ordinary aldehyde during a very cold winter; (3) a fluid modification, boiling at 125°, prepared by Weidenbusch[3] by the action of very dilute sulphuric or nitric acid on ordinary aldehyde, and to which Gerhardt gave the name paraldehyde; (4) the solid

[1] Chemische Briefe. [2] Ann. Chem. (Liebig) 27, 3[illegible] [3] *Ibid.* 66, 152.

modification, discovered by Liebig[1] and afterwards studied by Fehling and by Weidenbusch; (5) acraldehyde, formed by the action of zinc chloride on glycol or on ordinary aldehyde, discovered by Wurtz[2] and afterwards investigated by Bauer.[3] This last modification, acraldehyde, was later shown by Kekulé[4] to be a mixture of crotonic aldehyde and water.

The other modifications were more closely investigated by Geuther and Cartmell[5] and by Lieben.[6] The former prepared a polymeric modification, melting at $+10°$ and boiling at 124°, which they called elaldehyde, by the action of sulphur dioxide on aldehyde. Lieben also obtained a modification, boiling at 123°–124°, by heating aldehyde with ethyl iodide, as well as by the action of cyanogen on aldehyde. All three of these chemists are of the opinion that the polymeric substances obtained by Fehling and by Weidenbusch are identical with those prepared by them.

In their famous investigation, "Ueber das sogenannte Chloraceten und die polymeren Modificationen des Aldehyds," Kekulé and Zincke[7] showed that only two true polymeric modifications of ordinary aldehyde exist, viz. the fluid, paraldehyde, and the solid, metaldehyde. They also state that carefully purified aldehyde suffers no change on heating or on cooling or when kept for any length of time. Polymerization of the aldehyde, according to them, is always connected with the presence of certain substances, such as hydrochloric acid, sulphuric acid and carbonyl chloride, which appear to exert a sort of ferment-like action on the aldehyde, converting it into its polymers. In most cases both polymeric modifications are formed at the same time, the metaldehyde being produced most readily in the cold (below 0°), while the paraldehyde is formed at ordinary or higher temperatures.

The vapor-density of paraldehyde, determined by Fehling and by Weidenbusch, as well as by Kekulé and Zincke, is three times that of ordinary aldehyde, so that the formula of paraldehyde is $(C_2H_4O)_3$ or $C_6H_{12}O_3$. The results obtained later by Paternò and Nasini,[8] using the cryoscopic method, are also in accord with this formula.

According to Weidenbusch, paraldehyde, when distilled with a little sulphuric acid, yields ordinary aldehyde as the only product. Kekulé and Zincke confirmed this fact and showed that

[1] Ann. Chem. (Liebig) **14**, 141. [2] *Ibid.* **108**, 84. [3] *Ibid.* **117**, 141.
[4] *Ibid.* **162**, 77. [5] *Ibid.* **112**, 16. [6] *Ibid.* Suppl. Bd. 1, 114. [7] *Ibid.* **162**, 141.
[8] Ber. d. chem. Ges. **19**, 2529.

other substances, such as hydrochloric acid, carbonyl chloride, zinc chloride, and, in general, all those substances which polymerize ordinary aldehyde, bring about this same re-formation of aldehyde. With phosphorus pentachloride, paraldehyde gives ethylidene chloride,[1] and with hydrochloric acid, ethylidene oxychloride,[2] the same products which result when the simple aldehyde is treated with these reagents. But though paraldehyde reacts in general like the simple aldehyde, it does not show the characteristic aldehyde reactions; it does not reduce an ammoniacal solution of silver nitrate, does not resinify when boiled with a solution of potassium or sodium hydroxide, nor does it unite with either ammonia or with sodium bisulphite. Its molecule, therefore, cannot contain the characteristic aldehyde group $-\overset{\displaystyle H}{\underset{|}{C}}=O$.

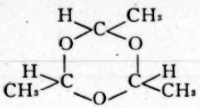
Regarding the structural formula of paraldehyde, Kekulé and Zincke[3] say: "The molecular formula of paraldehyde is, without doubt, $C_6H_{12}O_3$. From its conduct towards phosphorus pentachloride, acetic anhydride, hydrochloric acid, sulphuric acid, and in general towards all the ferment-like bodies which readily convert it into aldehyde, one may safely conclude that in it the aldehyde molecules are joined by means of oxygen in the form of a ring, as has been already assumed by different chemists for a long time.

"The view of Lieben,[4] that paraldehyde is a compound analogous to the acetals, *i. e.* an acetylethyl ether of ethylidene glycol, is contradicted by the facts. A body so constituted must give with acetic anhydride, besides the diacetate obtained by Geuther,[5] ethyl acetate; and with phosphorus pentachloride it must give ethyl chloride and acetyl chloride, in addition to ethylidene chloride."

According to Kekulé's view of the constitution of paraldehyde, its formation must take place by the union of three bivalent aldehyde residues, $CH_3-\overset{\displaystyle H}{\underset{|}{\overset{|}{C}}}-O-$ resulting from the action of the

[1] Geuther: Ztschr. Chem. 1865, 32.
[2] Kekulé and Zincke; Lieben: Ann. Chem. (Liebig) **106**, 336.
[3] Ber. d. chem. Ges. **3**, 468; Ann. Chem. (Liebig) **162**, 150.
[4] *Loc. cit.* [5] *Loc. cit.*

various polymerizing agents on the simple aldehyde, which leads to the following structural formula:



This formula is in strict accord with all the facts known, and has, moreover, received experimental confirmation at the hands of Brühl,[1] who showed that the molecular refraction of paraldehyde was $M_A = 52.48$, while that required by the above formula is $M_A = 52.77$. Paraldehyde does not react with phenylhydrazine nor with hydroxylamine, facts which are also in accord with the above formula.

The solid polymer, metaldehyde, is formed from aldehyde by the action of the same polymerizing agents that bring about the formation of paraldehyde, a low temperature being most favorable for its production. Only a small part of the aldehyde is converted into metaldehyde. Paraldehyde is always formed simultaneously with the metaldehyde and in much larger quantity. Metaldehyde differs from paraldehyde only in its *physical* properties, such as melting-point, crystalline form, solubility, volatility, etc. In its chemical conduct towards various reagents it acts exactly like paraldehyde; thus it is partly converted into aldehyde on heating, and undergoes complete dissociation when heated in the presence of substances which polymerize the simple aldehyde. Like paraldehyde, it is not acted on by caustic alkalies or by oxidizing agents. It does not reduce an ammoniacal solution of silver nitrate, unites with neither ammonia nor sodium bisulphite, nor does it react with hydroxylamine or phenylhydrazine. Hence it does not contain the aldehyde group $-\overset{H}{\overset{|}{C}}=O$. When it does react chemically it forms the same products that result from the action of the same reagents on aldehyde, probably owing to the re-formation of aldehyde in the presence of these substances; thus with phosphorus pentachloride it forms ethylidene chloride, and with chlorine, chloral. Its conduct towards small amounts of hydrochloric acid gas is especially noteworthy.

[1] Ann. Chem. (Liebig) **203**, 44. See also in this connection Ber. d. chem. Ges. **24**, 657.

According to Kekulé and Zincke,[1] hydrochloric acid gas in contact with metaldehyde changes it gradually into *paraldehyde* containing some aldehyde. Troeger[2] has noticed this same conversion of metaldehyde into paraldehyde, but in the case cited by him it took place apparently spontaneously.

Regarding the molecular weight and structural formula of metaldehyde comparatively little is known. The substance undergoes partial dissociation into ordinary aldehyde when heated, and hence the vapor-density determinations made by Liebig,[3] Hofmann,[4] and Kekulé and Zincke[1] gave unsatisfactory results. In this connection Kekulé and Zincke state "that since the vapor-density of metaldehyde is not known and the molecular weight cannot be determined by any of the facts now in our possession, nothing definite can be said concerning its constitution. The formation of ethylidene chloride and the easy transformation into the simple aldehyde make it probable that several aldehyde molecules (perhaps two) are here joined by oxygen to form a more complex molecule." The formula of metaldehyde is therefore generally given in treatises on chemistry as $(C_2H_4O)_x$, indicating that the molecular weight is unknown.

The vapor-density and consequently the molecular weight of metaldehyde have, however, been determined by Hanriot and Œconomedes,[5] both by the Dumas and the Hofmann methods. This they accomplish by ingeniously introducing a correction for the amount of metaldehyde-vapor converted into aldehyde and thus determining the true vapor-density of the undissociated metaldehyde. Their results by both methods lead to the same conclusion, viz. that the vapor-density and the molecular weight of metaldehyde are the same as those of paraldehyde. According to them, therefore, the formula for metaldehyde is the same as that of paraldehyde: $(C_2H_4O)_3$ or $C_6H_{12}O_3$. Hanriot and Œconomedes offer no explanation of this peculiar isomerism, which, if their results be correct, exists between paraldehyde and metaldehyde, but content themselves simply with the publication of the results.

Meldola and Streatfield[6] endeavored to determine the molecular weight of metaldehyde from the depression of the freezing-point

[1] Ann. Chem. (Liebig) **162**, 149.
[2] Ber. d. chem. Ges. **25**, 3316.
[3] Ann. Chem. (Liebig) **14**, 141.
[4] Ber. d. chem. Ges. **4**, 590.
[5] Ann. chim. phys. [5] **25**, 228.
[6] Chem. News **60**, 66 and 67 (1889).

of solutions of metaldehyde in glacial acetic acid, but with negative results—owing probably to the slight solubility of the metaldehyde in this solvent.

Quite recently—while we were engaged on this investigation, indeed—Zecchini[1] published a paper on the molecular weight of metaldehyde, in which he criticises the results of Hanriot and Œconomedes, and gives the results which he obtained using the boiling-point and freezing-point methods. With ether as a solvent he obtained very discordant results, which he thinks were due to the very slight solubility of the metaldehyde in this liquid. From the results obtained from the rise of the boiling-point of alcoholic solutions, he states it would be impossible to conclude precisely what is the true formula of metaldehyde, but asserts, nevertheless, that in alcoholic solutions its molecular weight is considerably higher than that required by the formula $(C_2H_4O)_3$. The formula would indeed seem to be, he says, not less than $(C_2H_4O)_6$. In solution in chloroform his results point to the same formula $(C_2H_4O)_6$, while in solution in phenol they lead to a formula intermediate between $(C_2H_4O)_3$ and $(C_2H_4O)_4$. Zecchini concludes his paper by saying that it is probable that the solid compound called metaldehyde has a high molecular complexity, and that, under certain circumstances, its molecules are separated into simpler molecules, perhaps corresponding to other polymers not yet isolated. Perhaps it would be advantageous, he continues, to repeat the experiments of Hanriot and Œconomedes, varying the quantity of the substance which is converted into vapor, and the conditions of temperature and pressure; probably formulas different from those proposed by them would be found.

It will be seen from this review of the literature of the subject that while the molecular weight and structural formula of paraldehyde have been accurately determined, and all the methods of finding the molecular weight which have been used in the case of paraldehyde give concordant results, the molecular weight of metaldehyde is still in doubt, and, of course, the structural formula of the substance is unknown. In order to determine the molecular weight of metaldehyde and, if possible, the relations existing between it and paraldehyde and the simple aldehyde from which both are derived, the present investigation was undertaken.

[1] Gazz. chim. ital. **22**, 586.

Experimental.

To determine the molecular weight of metaldehyde we have made use of the cryoscopic method of Raoult, as well as of the vapor-density method of Hofmann. Preliminary experiments soon showed that phenol and thymol were the best solvents for metaldehyde, and that the metaldehyde underwent absolutely no dissociation in these solvents. This was proved by dissolving a weighed quantity of the metaldehyde in the liquid solvent, determining the depression of the freezing-point several times, then treating the solution with ether and dissolving out the solvent, phenol or thymol, and recovering the metaldehyde. It was found that the metaldehyde could thus be recovered quantitatively. Any dissociation of the metaldehyde would have been immediately shown by a change in the freezing-point of the solution. In every case the freezing-point was determined a number of times and no change was noted, so that it may be assumed that no dissociation of the metaldehyde takes place in either phenol or thymol.

The metaldehyde was made according to the method given by Kekulé and Zincke. Pure paraldehyde was mixed with a few drops of concentrated sulphuric acid and distilled, the vapors passing through a Hempel distilling-tube one meter long filled with beads, to condense and return the undecomposed paraldehyde. The aldehyde thus formed was condensed by passing it through a long Liebig's condenser and into a receiver connected with the condenser by means of a bent adapter. The receiver was surrounded with a freezing-mixture of ice and concentrated hydrochloric acid. A few bubbles of hydrochloric-acid gas were then passed into the aldehyde still surrounded by the freezing-mixture. Crystals of the metaldehyde began to separate out at once. After allowing the mixture to stand for half an hour these were filtered off (using a Witt plate and suction to drain thoroughly), and washed with alcohol and ether and dried on filter-paper. As the filtrate still had a strong odor of aldehyde, it was again treated with hydrochloric acid gas and another crop of metaldehyde crystals obtained. The filtrate, consisting now of paraldehyde alone, was distilled with sulphuric acid and the aldehyde regained was again subjected to the above treatment.

An examination of the metaldehyde crystals under the microscope showed that they were filled with inclusions of liquid, either paraldehyde or aldehyde, and when they were ground to powder the odor of paraldehyde was distinctly perceptible. The metaldehyde used for the molecular-weight determinations was therefore recrystallized several times from boiling chloroform, in which it is soluble to the extent of about four per cent. The metaldehyde undergoes dissociation into the simple aldehyde very rapidly in warm chloroform solution, so that it is expedient in recrystallizing metaldehyde to dissolve the metaldehyde in the boiling chloroform, filter quickly and cool the clear filtrate in ice-water. The crystals of metaldehyde formed in this way were small and needle-shaped. They contained no liquid inclusions, and when ground gave no odor of either paraldehyde or aldehyde. When separated from the chloroform solution and spread out on drying-paper, the solvent evaporates very rapidly and leaves the metaldehyde crystals in a very desirable form for further work.

The crystals of the recrystallized metaldehyde were then ground to powder in an agate mortar and made up into the form of compressed tablets in the usual manner. Only the freshly crystallized metaldehyde was used in the following molecular-weight determinations, as it was found that metaldehyde undergoes decomposition on standing, being partially converted into paraldehyde, recognizable by its odor. We shall refer to this change later in this paper. Beckman's method, apparatus and thermometer were used in the freezing-point determinations, and in working with phenol solutions care was taken to exclude all moisture. This was done by means of the simple device used by us in the determination of the molecular weight of benzoyl peroxide[1] in glacial acetic acid. The results of the freezing-point determinations with the freshly crystallized metaldehyde follow.

Metaldehyde $(C_2H_4O)_3 = 132$.

Solvent, phenol;[2] molecular depression, 75; depression-coefficient, 0.5682.

[1] This Journal **15**, 353, and Ztschr. phys. Chem. **12**, 63.

[2] The phenol and thymol used in these determinations were prepared from the C. P. articles by redistillation. The purified products had the melting-points 41°–42° C. (uncorr.) and 49°–50° C. (uncorr.), respectively.

Wt. Solvent.	Wt. Sub.	Concentr.	Depress.	Dep.-coef.	Mol. Dep.	Mol. Wt. found.
20.45	0.0712	0.3481	0.206	0.5918	78.1	127
20.45	0.1615	0.7897	0.446	0.5647	74.5	133
20.45	0.2891	1.4136	0.799	0.5652	74.6	133
20.45	0.4187	2.0474	1.119	0.5465	72.1	137
21.86	0.1407	0.6434	0.332	0.5160	68.1	145
22.40	0.0578	0.2580	0.153	0.5930	78.3	126
22.40	0.1519	0.6781	0.363	0.5353	70.7	140
22.40	0.2686	1.2000	0.622	0.5183	68.4	145
25.24	0.1004	0.3978	0.219	0.5505	72.7	136

Solvent, thymol; molecular depression, 73.9; depression-coefficient, 0.5598.

Wt. Solvent.	Wt. Sub.	Concentr.	Depress.	Dep.-coef.	Mol. Dep.	Mol. Wt. found.
17.00	0.0780	0.4588	0.266	0.5800	76.5	128
17.00	0.1696	0.9976	0.558	0.5593	73.8	132
17.00	0.2892	1.7011	0.869	0.5108	67.4	145
21.12	0.1469	0.6955	0.375	0.5391	71.2	137

These results certainly show that the molecular weight of the freshly prepared metaldehyde is 132, or three times that of acetic aldehyde (44), and that consequently the formula of metaldehyde is the same as that of paraldehyde, $(C_2H_4O)_3$ or $C_6H_{12}O_3$.

Determination of the Vapor-density of Metaldehyde by the Hofmann Method.

Having thus shown that in solution in phenol and in thymol the freshly prepared metaldehyde is a trimolecular compound, we next repeated the work of Hanriot and Œconomedes, and endeavored to determine the density of metaldehyde-vapor by the Hofmann method. As has already been stated, metaldehyde undergoes partial dissociation into ordinary aldehyde when vaporized, so that to determine the vapor-density of metaldehyde by this method it becomes necessary to determine the weight and volume of the aldehyde formed by the dissociation of some of the metaldehyde in order to find the volume and weight of the metaldehyde-vapor remaining undissociated. To do this we proceeded as follows: a weighed quantity of the freshly crystallized metaldehyde was introduced into the inner tube of the Hofmann apparatus, which was then heated to the temperature of the vapor of boiling

aniline. The total volume occupied by the vapors of metaldehyde and aldehyde (formed by the dissociation of some of the metaldehyde) was then read off. The outer jacket of the Hofmann apparatus was then removed, and the inner tube cooled as quickly as possible to the temperature of the room to prevent a recombination of the aldehyde to form metaldehyde. The volume was again read off; this is the volume occupied by the aldehyde alone (which is, of course, a gas at this temperature and pressure), as all the metaldehyde remaining undissociated condenses at this temperature to a solid. Subtracting the second volume from the first—after having previously reduced both to the standard conditions of temperature and pressure, 0° C. and 760 mm.—we obtain the *volume* occupied by the undissociated metaldehyde-vapor at 0° C. and 760 mm. pressure. From the volume of the aldehyde we can easily deduce the weight by finding the volume at 0° C. and 760 mm., and multiplying this by the weight of one cubic centimeter of aldehyde-vapor. Subtracting this weight from the weight of the metaldehyde originally taken we get the *weight* of the metaldehyde remaining undissociated. We thus have the *weight* and the *volume* of the metaldehyde-vapor remaining undissociated, and can readily calculate from these the specific gravity of the metaldehyde-vapor referred to either air or hydrogen.

Practically, this determination of the density of the vapor of metaldehyde is not quite so simple. Owing to the fact that it is almost impossible to get all the air and moisture out of the inner tube, even though the mercury be heated to 300° C. previous to using it, it was found necessary to heat the inner tube to the temperature of the experiment, and take readings before introducing the metaldehyde. This enabled us to make a correction for the very small amount of gas present at the beginning of the experiment. While still at this temperature the metaldehyde is introduced,[1] and when this is entirely vaporized and the temperature has become constant, the necessary readings are again made. The outer jacket is then removed and similar readings taken when the gas has cooled to the temperature of the room. Corrections were introduced for the tension of mercury-vapor at the boiling-point of aniline as well as for that of the solid metaldehyde at the temperature of the room. The barometric height was taken by means

[1] By means of a small glass capsule made from a short piece of wide glass tubing closed at one end. The powdered metaldehyde was packed into this by means of a glass rod with rounded edges.

of a siphon-barometer located in the same room, and all mercury readings were corrected for temperature-changes. The inner tube of the Hofmann apparatus was graduated in cubic centimeters and carefully calibrated. Readings on this tube were taken by means of a pendulum-cathetometer in the usual manner.

We endeavored to determine the density of metaldehyde-vapor at temperatures different from those used by Hanriot and Œconomedes, but did not succeed on account of the fact that metaldehyde is not entirely converted into vapor until the temperature of the vapor of boiling aniline is reached, and higher temperatures cause its complete dissociation into the simple aldehyde.

The formulas used in reducing the observed volumes to standard conditions, and containing all the corrections above enumerated, are the following:

$$\text{I.}\quad V_0 = \frac{v\left[\frac{P}{1+.00018t} - \left(\frac{p''}{1+.00018t''} + \frac{p'}{1+.00018t'} + s\right)\right]}{760\,(1+at')}$$

$$\text{II.}\quad V_0 = \frac{v\left[\frac{P}{1+.00018t} - \left(\frac{p}{1+.00018t'} + \varepsilon\right)\right]}{760\,(1+at)}.$$

Formula I was used to calculate the volume v_0' (very small), due to the small amount of air and moisture contained in the mercury at the beginning of the experiment, and the total volume v_0'', after the introduction of the metaldehyde; formula II, to calculate the volume, v_0''', of the aldehyde resulting from the partial dissociation of the metaldehyde. v', v'' and v''' are the observed volume at the beginning, the total volume, and that of the aldehyde respectively.

t = the temperature of the room.

t' = the temperature of the aniline-vapor in the inner tube.

t'' = the mean temperature = $\frac{t+t'}{2}$.

P = the barometric pressure.

p' = the height of the mercury column within the vapor-jacket at the temperature t'.

p'' = the height of the mercury column below the vapor-jacket at the temperature t''.

p = the height of the mercury column in the inner tube at the temperature t.

s = the tension of mercury-vapor at the temperature t'.

ε = the tension of metaldehyde—about 1.2 mm. between 20°–25° C.

$(v'''_0 - v'_0)$ = the volume occupied by the aldehyde-vapor at 0° C. and 760 mm.

$(v'''_0 - v'_0) \times 0.00197076$ = the weight of the aldehyde-vapor $= w$.

$(v'_0 - v'''_0) = X$, the volume occupied by the undissociated metaldehyde-vapor at 0° C. and 760 mm.

W = the weight of the metaldehyde taken.

x = the weight of the metaldehyde remaining undissociated $= W - w$.

$\alpha = 0.00367$.

0.00018 = the coefficient of expansion of mercury.

The following are the readings[1]:

	I.	II.
W	0.0357 gram	0.0325 gram
P'	739.3 mm.	745.6 mm.
$p'_{w'}$	570.5 mm.	554 mm.
$p''_{w'}$	154.5 mm.	191 mm.
v'	41.3 cc.	38.6 cc.
$t_{w'}$	19.6°	22.2°
$t'_{w'}$	180.9°	180.7°
$t''_{w'}$	100.3°	101.4°
s	11 mm.	11 mm.
$P_{w''}$	739.3 mm.	745.6 mm
$p'_{w''}$	302.1 mm.	336.6 mm.
$p''_{w''}$	183.0 mm.	187.9 mm.
v''	85 cc.	78.2 cc.
$t_{w''}$	19.6°	22.2°
$t'_{w''}$	180.9°	180.7°
$t''_{w''}$	100.3°	101.4°
$P_{w'''}$	739.3 mm.	745.6 mm.
$p_{w'''}$	555.3 mm.	591.0 mm.
v'''	72.3 cc.	66.1 cc.
$t_{w'''}$	19.6°	22.2°
$t'_{w'''}$	21.5°	20.6°
ε	1.2 mm.	1.2 mm.
x	0.00535 gram.	0.00873 gram.
X	0.93 cc.	1.39 cc.

[1] The subscripts v', v'' and v''' indicate the readings for the observed volumes v', v'' and v'''.

Whence we deduce the vapor-density:

	Found. I.	Found. II.	Calculated Density for $(C_2H_4O)_3$.
Referred to air	4.45	4.85	4.57
Referred to hydrogen	64.22	70.12	66.00

Hanriot and Œconomedes give the following figures as the results of their determinations:

By the Dumas method:

	I.	II.	Calculated.
Density referred to hydrogen	72.2	63.7	66.00

By the Hofmann method:

	I.	II.	III.	IV.
Density referred to hydrogen	59.1	63.45	59.85	67.45

We have recalculated the results given by Hanriot and Œconomedes from their data and find that unless they have introduced corrections of which they make no mention, these are not quite so accurate as they appear to be. After eliminating some mistakes, plainly typographical errors, we have deduced the following values:

Dumas method:

	I.	II.
Density referred to hydrogen	69.6	...[1]

Hofmann method:

	I.	II.	III.	IV.
x (grams)	0.01538	0.0085	0.0109	0.0075
X (cc.)	3.1	1.39	2.13	1.55
Density, H=1	55.38	68.20	57.06	54.00

The results of the vapor-density determinations made by Hanriot and Œconomedes as well as those made by us, it will be seen, agree with the molecular weights deduced from the depression of the freezing-point of solutions in phenol and thymol, so that we must conclude that the freshly prepared metaldehyde has the same molecular weight and the same formula as paraldehyde.

Zecchini[2] made an attempt to determine the molecular weight of metaldehyde by the use of the boiling-point method. He used as solvents alcohol and chloroform, and gives the following results:

[1] It is impossible to recalculate the density from the figures given by H. and Œ. in experiment No. 2, by this method, owing to the fact that the authors have plainly inserted the wrong data.

[2] Gazz. chim. ital. **22**, 586.

I. Metaldehyde in alcohol; molecular rise, 11.5°.

Concentr.	Rise.	Coef. of Rise.	Mol. Rise.		
1.2742	0.03°	0.02355	11.40	for	$(C_2H_4O)_{11}$
1.3296	0.075	0.04348	11.48	"	$(C_2H_4O)_6$
2.8035	0.06	0.03316	11.70	"	$(C_2H_4O)_8$
1.9725	0.053	0.02656	11.81	"	$(C_2H_4O)_{10}$

II.[1] *Metaldehyde in chloroform;* molecular rise, 36.6°.

0.9100	0.14	0.1648	36.25	for	$(C_2H_4O)_3$
1.2779	0.22	0.1721	36.86	"	$(C_2H_4O)_3$
1.2957	0.16	0.1389	36.67	"	$(C_2H_4O)_6$
1.7716	0.24	0.1355	36.00	"	$(C_2H_4O)_6$

From the foregoing results, Zecchini concludes that metaldehyde has a molecular weight larger than that represented by the formula $(C_2H_4O)_3$, and that under certain conditions these complex molecules break down into simpler ones. He nowhere mentions the conditions of pressure under which his experiments were conducted. This, together with the fact that metaldehyde undoubtedly undergoes dissociation when its solutions are heated, would, we think, be sufficient to account for the discordant results which he obtained. It is difficult to understand how he could have drawn any conclusion from such results.

Earlier in this paper mention was made of the fact that in making molecular-weight determinations of metaldehyde, it was necessary to use freshly crystallized metaldehyde, as metaldehyde which had stood for any length of time was found to have undergone some sort of decomposition, forming paraldehyde as one of the products. We have investigated this decomposition very carefully and have proved that metaldehyde, far from being a very stable compound as most investigators have stated, is an exceedingly unstable substance, undergoing decomposition in some cases within twenty-four hours after it is prepared.

In order to determine the course of this decomposition as well as the products formed, we have made molecular-weight determinations of the decomposition-product both by the cryoscopic and the vapor-density methods.

Several samples of material were used for this purpose. One was a sample of metaldehyde which had been prepared two years

[1] At our request, Mr. B. H. Hite, at the Johns Hopkins University, repeated this work, but could get no constant results.

before by one of us, and had been kept in a tightly closed bottle ever since; the other was prepared by recrystallizing some of the metaldehyde recently made by us, from chloroform, and allowing the crystallized product to stand for about two weeks. One or two individual determinations were made with recrystallized metaldehyde, which had stood from one to three days after crystallizing. In making these determinations we proceeded as follows: the solid metaldehyde was pulverized in an agate mortar and allowed to stand, spread out on drying-paper for a short time until the odor of paraldehyde had completely disappeared. This odor of paraldehyde was found to be characteristic of metaldehyde which had been kept for any length of time, when it was powdered. After the product had lost the odor of paraldehyde it was made up into compressed tablets in the usual manner, and the molecular weight determined in solution in phenol and in thymol by the Beckman method. In working with phenol solutions care was taken to exclude all moisture in the manner already described. The results were almost identical in the several cases and were as follows:

Sample of metaldehyde which had stood two years:

$$(C_2H_4O)_4 = 176.$$

Solvent, phenol; molecular depression, 75; depression-coefficient, 0.4261.

Wt. Solvent.	Wt. Sub.	Concent.	Depress.	Dep.-coef.	Mol. Dep.	Mol. Wt. found.
19.78	0.1966	0.9939	0.458	0.4608	81.1	163
19.78	0.3160	1.5975	0.731	0.4576	80.5	164
18.61	0.0946	0.5083	0.228	0.4483	78.9	167
18.61	0.2032	1.0919	0.490	0.4487	78.9	167
18.61	0.3115	1.6738	0.769	0.4594	80.8	163
19.65	0.0987	0.5023	0.229	0.4557	80.2	165
19.65	0.2174	1.1063	0.522	0.4718	83.0	159
19.65	0.3350	1.7048	0.810	0.4751	83.6	158
19.65	0.4584	2.3328	1.110	0.4758	83.7	158
19.65	0.6195	3.1527	1.494	0.4738	83.4	159

Metaldehyde recrystallized from chloroform and allowed to stand for two weeks:

19.00	0.0756	0.3979	0.182	0.4574	80.5	164
19.00	0.1535	0.8079	0.365	0.4517	79.5	166
19.00	0.2443	1.2858	0.580	0.4511	79.4	166
19.00	0.4560	2.4000	1.104	0.4600	80.9	163

Metaldehyde recrystallized from chloroform and allowed to stand for two or three days:

22.40	0.1212	0.5410	0.233	0.4306	75.8	174

Solvent, thymol; molecular depression, 73.9; depression-coefficient, 0.4199.

Metaldehyde recrystallized from chloroform and allowed to stand for two or three days:

17.78	0.1047	0.5888	0.253	0.4296	75.6	172

It will be seen from these determinations that the *solid* material remaining when metaldehyde is allowed to stand has the molecular weight 176 and the formula $(C_2H_4O)_4$. It is made up of four aldehyde molecules and might be called tetraldehyde.

The results in nearly every case are a little lower than the theoretical values. This is probably due to the fact that the solid material still contained some paraldehyde. That this was the case was proved by powdering some of the compressed tablets which had stood for half an hour, when the odor of paraldehyde was quite apparent.

The change which metaldehyde undergoes on standing was also noticed by Troeger,[1] who found that when metaldehyde had been kept some time it was largely converted into paraldehyde and aldehyde. The same observation has been made by Friedel,[2] also by Mr. Kortright, in this laboratory. Troeger states that the solid substance remaining was metaldehyde, and he claims to have shown this by molecular-weight determinations of the substance in solution in phenol. He gives no results, however, and he also states that the results were not quite satisfactory, probably on account of the dissociation of the metaldehyde in the warm phenol. We have shown that metaldehyde undergoes no dissociation either in phenol or thymol solution during the determination of its molecular weight in these solvents, and we think that Troeger's unsatisfactory results were due to the fact that he had a mixture of the trimolecular compound, paraldehyde, and the tetramolecular compound $(C_2H_4O)_4$, formed by the spontaneous decomposition of the metaldehyde.

It is quite probable that the same explanation applies in the case of the results obtained by Zecchini in determining the molecular weight of metaldehyde in solution in phenol. He states that the experiments with phenol solutions would lead to the formula

[1] Ber. d. chem. Ges. **25**, 3316. [2] Bull. Soc. chim. (Paris) **9**, 384.

$(C_2H_4O)_4$, or, better, to a formula between $(C_2H_4O)_3$ and $(C_2H_4O)_4$. This is exactly what we should expect if metaldehyde which had stood for some time were used. For we have shown that such metaldehyde is a mixture of paraldehyde and the tetramolecular compound $(C_2H_4O)_4$. Zecchini makes no statement regarding the purity of his metaldehyde, nor did he recrystallize it. We are justified therefore in concluding that he used metaldehyde which had stood for some time, and was probably a mixture of paraldehyde and the tetramolecular compound $(C_2H_4O)_4$.

The results obtained from the depression of the freezing-point of solutions in phenol and thymol were then confirmed by vapor-density determinations, using the Hofmann method and apparatus. The same precautions were used as in the determination of the vapor-density of the freshly crystallized product.

Metaldehyde freshly crystallized from chloroform was allowed to stand for about two weeks. It was then pulverized and kept for some time until the odor of paraldehyde was no longer perceptible. The vapor-density was then determined in the manner already described. The data and results follow:

	I.		II.		III.	
W	0.0400	gram	0.0434	gram	0.0368	gram
P_v	737	mm.	739	mm.	738	mm.
p'_v	528	mm.	538	mm.	557	mm.
p''_v	201	mm.	199	mm.	183	mm.
v'	41.5	cc.	39.7	cc.	39.4	cc.
t_v	20.8°		19.1°		20°	
t'_v	180°		180.1°		179.7°	
t''_v	100.4°		99.6°		99.8°	
s	11	mm.	11	mm.	11	mm.
$P_{v'}$	737	mm.	739.4	mm.	738	mm.
$p'_{v'}$	285.4	mm.	279	mm.	310	mm.
$p''_{v'}$	197.5	mm.	198	mm.	179.5	mm.
v''	86	cc.	86.8	cc.	84.6	cc.
$t_{v'}$	20.8°		19.6°		20°	
$t'_{v'}$	180°		180.1°		179.7°	
$t''_{v'}$	100.4°		99.6°		99.8°	
$P_{v''}$	737	mm.	739.4	mm.	738	mm.
$p_{v''}$	556.5	mm.	554	mm.	557.5	mm.
v'''	72.6	cc.	72.8	cc.	72.2	cc.
$t_{v''}$	20.8°		19.6°		20°	
$t_{v''}$	20°		19°		19°	
ϵ	1.2	mm.	1.2	mm.	1.2	mm.
x	0.00963	gram	0.01157	gram	0.00586	gram
X	1.34	cc.	1.52	cc.	0.76	cc.

Whence we deduce the vapor-density:

	Found. I.	II.	III.	Calculated Density for $(C_2H_4O)_4$.
Referred to air	5.56	5.90	5.96	6.09
" " hydrogen	80.22	84.98	86.05	88.00

These results show that metaldehyde undergoes decomposition when allowed to stand for some time, and that one of the products formed during this decomposition has the formula $(C_2H_4O)_4$. The other products are paraldehyde and a small amount of aldehyde, as Troeger and Friedel have already shown.

That this change of the metaldehyde into tetraldehyde, $(C_2H_4O)_4$, paraldehyde, and aldehyde, takes place in the dark as well as in the light, was shown by allowing some of the freshly recrystallized metaldehyde to stand in a desiccator of brown glass in a dark room for three days. It was then taken out and pulverized. The odor of paraldehyde was noticed, as in previous cases, when the metaldehyde was not kept in the dark, and molecular-weight determinations showed that the solid product remaining was tetraldehyde, $(C_2H_4O)_4$. Further investigation showed that this decomposition of the metaldehyde was increased by a rise in the temperature of the room. In this connection it should, perhaps, be stated that Friedel[1] succeeded in transforming more than half of the metaldehyde into a liquid consisting of paraldehyde mixed with a little ordinary aldehyde, by heating some grams of metaldehyde in a sealed tube to a temperature of 60°–65°. Friedel says nothing, however, about the solid product remaining after heating the metaldehyde.

This tetramolecular compound $(C_2H_4O)_4$, tetraldehyde, resembles metaldehyde very closely—so closely indeed that it was only discovered by making molecular-weight determinations with it in solution in phenol and in thymol. It has the same crystal form as metaldehyde, but differs from it in that the crystals are dull and opaque, while those of metaldehyde are clear and transparent. One may follow the change of metaldehyde into this tetramolecular compound, indeed, by noticing the change taking place in the crystals. This change takes place much more rapidly[2] in the product recrystallized from chloroform, than in the larger crystals formed by the action of calcium chloride on ordinary

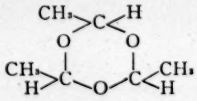
[1] *Loc. cit.*

[2] The change is apparent in some cases (where the temperature of the room is high) within twenty-four hours, though it is by no means complete within this time.

aldehyde. The freshly crystallized product is pulverized with difficulty ; the clear, transparent crystals, being tough and fibrous, merely pack together without becoming powdered. The tetraldehyde, on the contrary, is easily reduced to powder. The crystals have become brittle as well as dull and opaque, on standing. The solubility of the tetraldehyde in phenol and in thymol is much greater than that of metaldehyde. The tetraldehyde is soluble in warm chloroform to about the same extent as metaldehyde. Several attempts were made to recrystallize the tetraldehyde from chloroform, but without success, owing to the fact that the recrystallized product was found to have the same molecular weight and properties as the metaldehyde. It is quite probable that the tetraldehyde undergoes dissociation in solution in warm chloroform into the simple aldehyde, and that on cooling the hot chloroform solution in ice-water or in a freezing mixture —the method usually employed by us—metaldehyde crystallizes out, being the more stable form at this low temperature. That this is really the case seems likely, from the fact that the chloroform solution of the tetraldehyde has a strong odor of aldehyde, and is found to contain considerable quantities of paraldehyde when the crystals have been filtered out of the solution. The chemical conduct of the tetraldehyde is practically the same as that of metaldehyde with the same reagents. It is decomposed partially into the simple aldehyde when heated, and undergoes complete dissociation when heated in the presence of sulphuric or hydrochloric acid.

Theoretical.

Having thus shown that paraldehyde and metaldehyde are undoubtedly isomers as well as polymeric modifications of acetic aldehyde, and that metaldehyde is the unstable form, it yet remains to find some explanation of this peculiar kind of isomerism. Paraldehyde is certainly a ring-compound in which the oxygen atoms connect the various groups. The structural formula usually assigned to it,



is in strict accord with its formation from the simple aldehyde, its decomposition-products, and its chemical conduct in general, and may be regarded as correct. The recent work of Brühl[1] on the relation between the spectrometric constants and the chemical constitution of paraldehyde, points to this formula as the only one which will satisfy all the requirements. Metaldehyde has the same molecular weight and the same general formula as paraldehyde, $(C_2H_4O)_3$ or $C_6H_{12}O_3$. It is not possible to explain the isomerism existing between these two substances by any hypothesis which merely takes into consideration differences of structure in a plane. The plane structural formulas would indeed seem to be identical, as the chemical conduct of either isomer may be accurately represented by the same structural formula. After a complete and exhaustive study of the chemical conduct of these two substances, we have come to the conclusion that they are stereo-, or space-, isomers.[2] Some of the reasons that led to this conclusion are as follows:

1. Paraldehyde and metaldehyde contain the same elements, have the same percentage composition and the same molecular weight.

2. Both paraldehyde and metaldehyde are formed from acetic aldehyde by the action of the same polymerizing agents, a low temperature (below 0° C.) being favorable for the formation of metaldehyde; paraldehyde being formed under ordinary conditions. The unstable polymer, metaldehyde, is always formed in much smaller quantity than paraldehyde, and paraldehyde is always formed simultaneously with it.

3. The chemical conduct of both paraldehyde and metaldehyde is identical with the same reagents. Thus, with phosphorus pentachloride both give ethylidene chloride, while with hydrochloric acid both yield ethylidene oxychloride. Both remain unchanged when boiled with strong alkalies, and neither reacts with ammonia, hydrocyanic acid, sodium bisulphite, hydroxylamine or phenylhydrazine. Neither reduces Fehling's solution or an ammoniacal solution of silver nitrate. The formulas for these two substances must then show that they are identical so far as chemical conduct

[1] Ber. d. chem. Ges. **24**, 653.

[2] Meyer and Jacobson in their "Lehrbuch der organischen Chemie," suggest that paraldehyde and metaldehyde may be stereoisomers. Friedel makes the same suggestion in a paper (Bull. Soc. chim. (Paris) [3] **9**, 384) which appeared after the work here recorded had been completed.

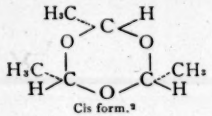
is concerned, and that they do not contain the characteristic aldehyde group $-\overset{O}{\overset{\|}{C}}-H$.

4. Kekulé and Zincke showed that metaldehyde in contact with a small amount of hydrochloric-acid gas is converted into paraldehyde containing some aldehyde. Troeger and Friedel have both observed that in some cases this change takes place spontaneously. We have noted above that metaldehyde can only be kept a short time owing to its liability to change into paraldehyde and the tetramolecular compound $(C_2H_4O)_4$, and have shown that this change is a function of the temperature.

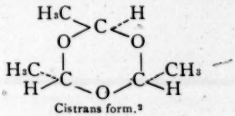
5. Both paraldehyde and metaldehyde are decomposed when heated with the same reagents that bring about their formation from acetic aldehyde, and both yield the same product, viz., acetic aldehyde.

All these facts point to the conclusion that we have here to deal with a simple case of stereo-, or geometrical, isomerism, of the same kind as that to which Baeyer referred the hexahydroterephthalic acids.

Referring now to the structural formula by which we must represent both the molecule of paraldehyde and that of metaldehyde, it will be seen—more clearly by using models[1]—that it admits of two configurations in space, and only two:



Cis form.[2]



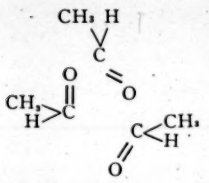
Cistrans form.[2]

the one corresponding to the cis or maleïnoid form, the other to the cistrans, or fumaroid form. A careful examination of the models will show that these two forms are the only ones possible.

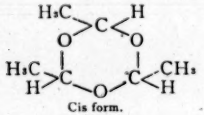
According to this view of the structure of metaldehyde and paraldehyde, the formation of these isomers from acetic aldehyde may be represented graphically as follows:

[1] The Kekulé models are well adapted for this purpose.

[2] The broken lines represent the groups below and the unbroken lines those above the plane of the paper.

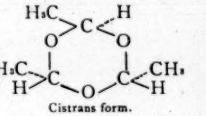


Three molecules of aldehyde uniting to form either



Cis form.

or



Cistrans form.

The next problem was to determine which of these stereo- or space-formulas corresponds to paraldehyde and which to metaldehyde. Two facts may be made use of to aid in solving this question: (*a*) the relative stability of the paraldehyde and metaldehyde, and (*b*) the relative amounts of paraldehyde and metaldehyde formed when acetic aldehyde undergoes polymerization. We should expect the cistrans form to be more stable than the cis form, if we reason from the conclusions derived from the study of other stereo-isomers, and if we take into consideration that in the cistrans form like groups or atoms which would have little or no attraction for each other, are represented as far away from each other as possible, while unlike groups, such as methyl and hydrogen—which would certainly exert some influence on each other—are represented as nearer to each other. The reverse is true in the cis formula. Here all the hydrogen atoms are represented on one side of the molecule and all the methyl groups on the other. The hydrogen atoms would exert no attraction on each other nor would the methyl groups influence the other methyl groups. Like groups or atoms are in other words nearer to each other in the cis form than in the cistrans form, and unlike groups or atoms are farther apart, so that this form would naturally be the unstable one and would tend to pass into the other, provided the conditions for the change are favorable. It has been demonstrated in the present paper that metaldehyde is the unstable polymeric modification of acetic aldehyde, and that it tends to pass

into paraldehyde, particularly in the presence of a halogen acid or when the temperature is raised. We therefore assign the cis formula to the unstable modification, metaldehyde, and the cistrans formula to paraldehyde, the more stable modification.

The second consideration is based on the theory indicating the relative amounts of the cis and the cistrans modifications that would be formed, provided the double bond between the carbon and oxygen atoms does not break preferably on the one side or other of the aldehyde molecule. It will be seen by referring to the models and to the graphical representation of the polymerization of aldehyde that the three molecules of aldehyde can give but two forms of the trimolecular compound, the cis and the cistrans. Each molecule of the aldehyde may combine with the other two, and as each molecule in the nascent condition has two bonds or free affinities, the total number of ways in which combination may take place will therefore be eight ($2\times 2\times 2=8$). Of these eight combinations six will be of the cistrans form, but only two of the cis form. The proportion of the cistrans modification and the cis modification formed by the polymerization of aldehyde should then be, so far as we can see, three parts of the cistrans form to one of the cis. No actual measurements of the exact amount of paraldehyde and metaldehyde formed in the polymerization of aldehyde have ever been made, but every one who has made metaldehyde knows that paraldehyde is always formed simultaneously with the metaldehyde and in much larger quantity. Kekulé and Zincke and many other chemists mention this fact which we have frequently confirmed. To paraldehyde therefore we give the cistrans formula, and to metaldehyde the cis formula.

The heats of combustion of paraldehyde and of metaldehyde have been determined by Louguinine,[1] and have been found to be nearly the same at constant pressure. The figures actually obtained were 813200 calories for paraldehyde and 805790 calories for metaldehyde. This difference in the heats of combustion of these two isomers is attributed by Louguinine to differences in the physical conditions of the two substances, but it seems more likely that it is due to the fact that paraldehyde is the more stable modification of the two, and this being the case it would probably, though not necessarily, give out more heat on combustion. The experi-

[1] Compt. rend. **108**, 620.

ment of Friedel, moreover, shows that to pass from the metaldehyde condition to that found in paraldehyde it is necessary to add energy in the form of heat. The study of the heats of combustion of paraldehyde and metaldehyde, then, show that paraldehyde is the stable form, while metaldehyde is the unstable form.

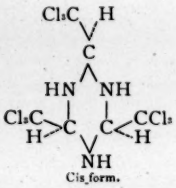
Perhaps it may be well to mention here some evidence confirmatory of this view of the relation existing between paraldehyde and metaldehyde. If these two substances are really stereo-isomers, then it will be seen by referring to the models that when the methyl groups of paraldehyde or metaldehyde are replaced by hydrogen there should be but one substance; there is no longer any possibility of stereo-isomerism. This means that formic aldehyde should give but one polymeric modification, having the formula $(CH_2O)_3$. Of the polymeric modifications that have been described, paraformic aldehyde and α-trioxymethylene, only one, α-trioxymethylene, is a trialdehyde. In its properties both physical and chemical, it resembles paraldehyde very closely. The other polymer, paraformic aldehyde, will probably be found to have a greater molecular weight than the formula $(CH_2O)_3$ indicates, since it is insoluble and amorphous and does not have a constant melting-point. We may therefore state that the theory indicates the existence of only one triformic aldehyde, and that but one is known, α-trioxymethylene.

Again, if we replace the methyl groups in paraldehyde and metaldehyde by ethyl groups, we ought to have two stereo-isomers. A compound in which the methyl groups of paraldehyde and metaldehyde are replaced by ethyl groups, we should expect to result from the polymerization of propionic aldehyde, C_2H_5CHO. Two polymeric modifications of propionic aldehyde are indeed known, and so closely do they resemble paraldehyde and metaldehyde in their physical and chemical properties, that it is only by analysis or a molecular-weight determination that they can be distinguished. The facts and the theory are here again in accord. There are many other aldehydes which polymerize quite readily, and yield two varieties or forms of polymers. Polymerization indeed appears to be a characteristic property of the aldehydes. That these polymers, the trialdehydes, are related to each other in the same way that paraldehyde and metaldehyde are, there seems but little reason to doubt, but it will require further work to establish this hypothesis.

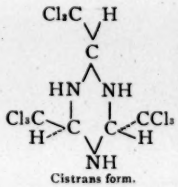
The polymeric thioaldehydes have been very thoroughly studied by Baumann and Fromm. These chemists have shown that trithioformic aldehyde exists in only one form, while the polymeric modifications of thioacetic aldehyde, trithioacetic aldehyde, exist in two stereo forms corresponding to the cis and the cistrans forms. The cis modification agrees with metaldehyde in every respect, even to the transformation into the cistrans modification by heating, or in the presence of strong hydrochloric acid.

Acetone contains the carbonyl group, and in most of its properties shows a striking analogy to the aldehydes. We should expect it to polymerize and yield but one triacetone $(C_3H_6O)_3$. Unfortunately it has not been found possible to make a polymeric modification of acetone, though many attempts have been made, owing probably to the ease with which it undergoes condensation in the presence of polymerizing-agents. Baumann and Fromm have, however, prepared a polymeric modification of thioacetone having the formula $(C_3H_6S)_3$, and have shown that it exists in but one form. By consulting the models it will be seen that stereo-isomerism is impossible here.

The recent work of Béhal and Choay[1] on chloralimide and isochloralimide also confirms the view that paraldehyde and metaldehyde are stereo-isomers. It will be seen from the formula of chloralimide, $CCl_3.CH=NH$, that, just as chloral itself and ordinary aldehyde contain the double union between the carbon and oxygen atoms, it contains the double union between the carbon and nitrogen atoms. From what we have learned of the polymerization of aldehyde, we should expect three molecules of this chloralimide to combine to form a trichloralimide, and this trichloralimide ought to exist in two forms corresponding to the formulas:



Cis form.



Cistrans form.

[1] Ann. chim. phys. [6] **26**, 34.

Béhal and Choay have shown that two forms exist and that one corresponds to the cis compound, the other to the cistrans, and that one may be converted into the other.

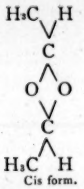
It is of interest to note that this polymerization of the aldehydes is in some way connected with the peculiar condition existing between the carbon and oxygen atoms, a condition which may be termed the unsaturated condition. In the case of the unsaturated hydrocarbons, with the exception of acetylene and ethylene, polymerization takes place very readily in the presence of sulphuric acid, thus allylene gives mesitylene, and dimethylacetylene hexamethylbenzene. Propylene, isobutylene and amylene all polymerize in the presence of sulphuric acid. This tendency towards polymerization is particularly noticeable also in the case of cyanogen compounds.

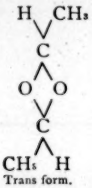
In the case of the formation of di-, tri- and tetramylene from amylene in the presence of sulphuric acid, it seems very likely that an addition-product is first formed and that this then breaks up into amylene and sulphuric acid. The amylene molecules being, as it were, in the nascent condition, unite to form the di-, tri-, and tetramylenes, as they are called. It seems quite likely that a similar process takes place here when polymeric modifications of the aldehydes are formed. Thus, in the case of acetic aldehyde and hydrochloric-acid gas, we may assume that an addition-product is first formed according to the equation:

$$CH_3CHO + HCl = CH_3CH\begin{matrix}OH\\Cl\end{matrix}.$$

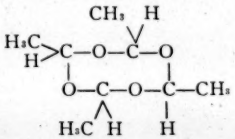
This hydrochloric-acid addition-product, being exceedingly unstable (as we know from the work of Hanriot and Œconomedes), loses hydrochloric acid, and three molecules of the nascent aldehyde thus formed combine to form either paraldehyde or metaldehyde, according to the conditions of the experiment. Adopting this view, it is easy to see why a few bubbles of hydrochloric-acid gas can convert a large quantity of aldehyde into paraldehyde and metaldehyde, for the hydrochloric acid is constantly regenerated.

There would seem to be no good reason why dialdehydes and tetraldehydes should not be produced also by a similar method of formation. The dialdehyde would have the formulas:


Cis form.


Trans form.

and would exist in the two forms, cis and trans. A dialdehyde, $(C_2H_4O)_2$, is indeed known, but whether it has one of the above formulas or not cannot now be stated. The tetraldehyde has been shown to exist also, and has in all probability a structural formula similar to that of paraldehyde, viz.,



This formula will explain all the facts now known about the tetraldehyde.

Summary.

Some of the results obtained in this work may be summed up as follows:

1. Paraldehyde and metaldehyde have the same molecular weight, and from their chemical conduct

2. Both must be represented by the same structural formula in a plane, but

3. The difference between them may be readily understood they are regarded as stereo-isomers:

4. Paraldehyde, the more stable modification, being the cistrans, while metaldehyde is the cis variety.

Further work to determine the correctness of this theory of the relation of the polymeric aldehydes is now being carried on in this laboratory.

Cornell University, Ithaca, N. Y., *June*, 1893.

Contributions from the Kent Chemical Laboratory of the University of Chicago.

THE ACTION OF PHOSPHORUS PENTACHLORIDE ON URETHANES.

By Felix Lengfeld and Julius Stieglitz.

In the course of our work on nitrogen halogen compounds we found that urethanes are easily obtained by the action of alcoholates on amide bromides (R.CO.NHBr),[1] and it seemed desirable to convert urethanes, prepared by this method, into the corresponding ureas. Attempts to prepare unsymmetrical ureas by substituting amidogen for alkoxyl in NHRCO–OR—making use of the direct action of ammonia on urethanes—have shown that at low temperatures there is no action, whereas at higher both the OR and NHR groups are replaced and urea results. The usual method of converting urethane into the amine and treating with potassium cyanate is not applicable to those urethanes whose amines cannot, on account of their instability, be obtained from them. Hofmann[2] showed that urethanes may be converted into isocyanates by heating with phosphorus pentoxide; and isocyanates unite with ammonia to form unsymmetrical ureas. We found that a mixture of phenylurethane and phosphorus pentoxide begins to react at 90°–95° and colors already at this temperature; it therefore seemed probable that the substitution of phosphorus pentachloride would enable us to work at lower temperatures and would avoid the formation of isocyanates which polymerize easily. The reaction promised to be interesting also as leading to a new method for preparing chlorformamides, R.NH.CO.Cl, or chlorformimido-ethers, $R.N{:}C\begin{matrix}Cl\\OR\end{matrix}$.

The action of chlorides on urethanes has been frequently investigated. M. Loeb[3] heated urethane to 75° with phosgene in benzene and obtained allophanic ether. Schroeter and Levinsk[4] found that thionyl chloride reacts on urethane to form allophanic ether; that it does not react on phenylurethane at low temperatures and carbonizes it at higher. Phosphorus trichloride and oxychloride gave no definite results.[5] A. Werner[6] obtained, by the action of phosphorus pentachloride on phenylurethane, phenylisocyanate alone.

[1] This Journal **15**, 504. [2] Ber. d. chem. Ges. **3**, 655. [3] *Ibid.* **19**, 2344.
[4] *Ibid.* **26**, 2171. [5] *Ibid.* **26**, 2173. [6] *Ibid.* **26**, 1565.

We tried first the action of phosphorus pentachloride on phenylurethane. 10 grams (1 molecule) phenylurethane were mixed with 12.5 grams (1 molecule) phosphorus pentachloride in a flask connected with a long upright tube ending in a calcium-chloride tube. There was no reaction in the cold. On warming slowly in a water-bath, the urethane melted at about 50°, and at 55° a gas, identified as ethyl chloride, was slowly evolved. Care was taken to prevent violent action by occasionally removing from the bath, and at no time was the temperature allowed to exceed 55°. The reaction was complete in ten to fifteen minutes. The flask was then put into a mixture of ice and salt, and ice-cold, sodium-dried ligroïn (boiling-point 40°–60°) added. An oil, which soon solidified to a mass of white crystals, separated. The crystals were quickly filtered off, washed with a little ligroïn (in which they are not very soluble), and brought on dry clay plates in a vacuum-desiccator. The substance melts at 53°–55°, and on heating, decomposes at 90°–100° into phenyl isocyanate and hydrochloric acid. It has the penetrating odor, irritating action and general properties of chlorformanilide. Analysis:

0.0769 gram substance ignited with lime and titrated by Volhard's method, gave 0.01745 gram chlorine.

	Calculated for C_7H_4NOCl.	Found.
Cl	22.83	22.69

Hentschel,[1] who prepared chlorformanilide by the action of hydrochloric acid on phenyl isocyanate, gives its melting-point as 45°. We prepared it by this method, using freshly distilled isocyanate and cooling at first with water. As soon as the mass solidified it was melted in a water-bath at 55° and the current continued for fifteen minutes. The powdered product was washed with dry ligroïn and placed on dry clay plates in a vacuum-desiccator. The compound melted at 58°–59°, and decomposed into hydrochloric acid and phenyl isocyanate at 90°–100°. The two substances are identical in every way excepting a slight difference in their melting-points. That the higher melting-point is the correct one is shown by chlorformanilide prepared in another way.[2] Hentschel's low melting-point may be due to the presence of unchanged isocyanate in his preparation, as indicated by his low figures. A little over three grams solid chlorformanilide was

[1] Ber. d. chem. Ges. **18**, 1178.

[2] *Vide* analysis, p. 74.

obtained from 10 grams phenylurethane, and more remained in solution in the phosphorus oxychloride and ligroïn filtered off. The crystallized substance reacts violently with concentrated aqueous ammonia, giving monophenylurea, which, on washing with cold water, drying and recrystallizing from boiling chloroform, melts at 144°–145°. On analysis:

0.1544 gram substance gave 27.5 cc. moist nitrogen at 743 mm. and 16.5°.

	Calculated for $C_7H_8N_2O$.	Found.
N	20.59	20.33

On shaking the ligroïn and phosphorus oxychloride filtrate from 10 grams urethane with concentrated aqueous ammonia, evaporating the ligroïn and washing with cold water, there were obtained 3 grams of monophenylurea, which after one crystallization melted at 142°. If it be desired to make monophenylurea from phenylurethane it is unnecessary to isolate the chlorformanilide. The crude product of the reaction between phosphorus pentachloride and phenylurethane is diluted with ligroïn or ether and poured gradually into concentrated aqueous ammonia. 10 grams of the urethane give about 6 grams of the urea, or about 75 per cent. of the theoretical yield. The whole operation for the preparation of the crude urea does not take over an hour.

The first action of phosphorus pentachloride on the acid amides[1] and on the ether[2] is the replacement of carbonyl oxygen by chlorine, giving compounds $R.C<^{NHR}_{Cl_2}$ and $R.C<^{OR}_{Cl_2}$. These are unstable, losing in the first case hydrogen chloride so easily that they cannot be obtained pure, and in the other splitting off alkyl chloride more or less readily. Phenylurethane being both an amide and an ether, must form an analogous compound:

$$C_6H_5.NH.COOC_2H_5 + PCl_5 = C_6H_5.NH.C<^{Cl_2}_{OC_2H_5}.$$

It seems as if such a compound could lose either hydrochloric acid or ethyl chloride. As a matter of fact ethyl chloride is given off:

$$C_6H_5.HN.C<^{Cl}_{O\,\boxed{Cl\ C_2H_5}} = C_6H_5.HN.C<^{Cl}_{O} + C_2H_5Cl.$$

[1] Wallach: Ann. Chem. (Liebig) **184**, f. [2] Anschütz: *Ibid.* **254**, 14.

This result is rather surprising, since hydrochloric acid is apparently split off from the chloramides more easily than alkyl chloride from dichlorglycolic ethers. Ethyl anilidochlorformate, $C_6H_5.N{:}C{<}^{Cl}_{OC_2H_5}$, as found in this laboratory by W. R. Smith, distils in a vacuum without decomposition at 115°–120°. Ethyl anilidochlorformate being similar in constitution to phenyl isocyanate, might unite with hydrochloric acid and thus form the desired intermediate product, which could then be isolated:

$$C_6H_5.N{:}C{<}^{Cl}_{OC_2H_5} + HCl = C_6H_5.NH.C{<}^{Cl_2}_{OC_2H_5}.$$

Our preliminary experiments indicate that an addition-product which loses ethyl chloride even at −15° is really formed.

Ethyl anilidochlorformate was first obtained by A. Werner[1] by the action of phosphorus pentachloride on ethylsynbenzhydroximic acid. It has also been made in this laboratory by W. R. Smith, working with J. U. Nef, by the prolonged digestion of phenylimidocarbonyl chloride in ether solution with sodium ethylate.

We found that it can be very easily prepared as follows: To 10 grams phenylimidocarbonyl chloride[2] dissolved in about 10 cc. absolute alcohol and 10 cc. dry ether and cooled to 0°, an ice-cold solution of 1.33 grams sodium (1 atom) in 20 grams absolute alcohol is gradually added, the liquid being at the same time shaken thoroughly and cooled with ice. Reaction takes place at once and is complete after ten minutes. The mixture is then poured into ice-water and at once exhausted with ether. It is best to treat the first ether-extract separately, if a pure product is desired; a second extraction exhausts the residue sufficiently. The ether solution is washed rapidly five or six times with small quantities of cold water to remove all alcohol, filtered and dried with calcium chloride. After twenty-four hours the solution is transferred by a siphon fitted with a filter to a beaker, and the ether is then removed in a vacuum-desiccator over potassic hydroxide. The reaction is quantitative as follows:

$$C_6H_5.N{:}CCl_2 + NaOC_2H_5 = C_6H_5.N{:}C{<}^{Cl}_{OC_2H_5} + NaCl,$$

[1] Ber. d. chem. Ges. **25**, 38; **26**, 1565.

[2] Easily obtained by the action of chlorine on phenyl mustard-oil.—Sell and Zierold: Ber. d. chem. Ges. **7**, 1228, and Nef: Ann. Chem. (Liebig) **270**, 284.

the aqueous washings being neutral or very slightly alkaline. The oil as obtained was perfectly colorless and of an agreeable odor. It may be kept for days over potassic hydrate unchanged, in the absence of light; in the air and over sulphuric acid it soon acquires the disagreeable odor of phenyl isocyanate, probably through the action of hydrochloric acid formed from the compound by moisture or sulphuric acid, on the vapors of the substance. For most purposes the oil is sufficiently pure. For analysis we passed dry air through it for half an hour at 20 mm. pressure and then distilled at this pressure. When pure, the oil distilled unchanged at 115°–120°; in the presence of even traces of impurities, more or less decomposition into ethyl chloride and phenyl isocyanate takes place. The distillate can be entirely freed from these products by a small current of dry air at 20 mm. pressure and 90°–100°.

Analysis: 0.3455 gram substance gave 0.2605 gram AgCl (Carius).

	Calculated for $C_9H_{10}NOCl$.	Found.
Cl	19.35	18.65

The low result is partly due to a slight decomposition in closing the bulb containing the fluid, and also to the fact that the oil analyzed had not been purified by the air-current at 100°. As Mr. Smith will describe the compound more fully and its identity is beyond question, we did not consider another analysis necessary.

Dry hydrochloric acid gas was passed into ethyl anilidochlorformate cooled to —12° or —15°. It is completely absorbed at first without any evolution of gas; after a while crystals are deposited, and an excess of acid carries through a gas not completely absorbed by potassic hydrate. To complete the reaction the mixture was kept fluid by warming to 40°–50° and the current continued for a few minutes. The gas given off proved to be ethyl chloride. On cooling, the residue solidified to a cake which was powdered under ligroïn and washed. The crystals melted at 58°–59°, give hydrochloric acid and phenyl isocyanate at 90°–100°, and proved in every respect identical with chlorformanilide.

Analysis: 0.2212 gram substance heated with lime and titrated according to Volhard, gave 0.05094 gram Cl.

	Calculated for C_7H_4NOCl.	Found.
Cl	22.83	23.03

The reaction is

$$C_6H_5.N{:}CCl(OC_2H_5) + HCl = C_6H_5.NH.COCl + C_2H_5Cl.$$

To show that the formation of ethyl chloride does not depend on an excess of hydrochloric acid, 0.085 gram hydrochloric acid (calculated, 0.126 gram) was passed into 0.635 gram ethyl anilidochlorformate at —12°. On warming, at 40°–50°, and yet more at 70°, ethyl chloride was given off. The loss was 0.140 gram; calculated, 0.150 gram for 0.085 gram hydrochloric acid. The residue solidified largely as chlorformanilide. The boiling-point of ethyl chloride being 12°, and the gas being given off only at 40°–70°, the experiment was repeated in a different manner, to determine whether an addition-product had been formed which loses ethyl chloride on warming, or whether the ethyl chloride was in solution and its boiling-point raised 30–60 degrees by the other compounds present: 0.165 gram hydrochloric acid (calculated, 0.271 gram) was slowly passed into 1.365 grams substance at —15°; crystals separated to some extent as before. The mixture was kept at —15° and connected with an air-pump; the pressure sank rapidly to 120 mm., then a gas was given off in quantity, the pressure rose 20–30 mm. and then sank gradually to 20 mm. The loss in weight was 0.260 gram; calculated for 0.165 gram hydrochloric acid, 0.290 gram ethyl chloride. The crystals separated from unchanged substance by placing on a clay plate proved to be chlorformanilide; they melted at 58°, decomposed at 100° into hydrochloric acid and phenyl isocyanate, and gave no ethyl chloride. This shows that if addition of hydrochloric acid takes place, the addition-product decomposes even at —15° into ethyl chloride and chlorformanilide. To prevent local superheating, we passed the acid into the substance diluted by neutral solvents. In ligroïn a crystalline deposit of chlorformanilide is gradually formed at —12°. 1 gram of ethyl anilidochlorformate was then dissolved in 2.7 grams absolute ether and cooled to —12°. Each bubble of hydrochloric acid causes an oily turbidity which settles to the bottom of the vessel for an instant, then disappears completely in the remaining fluid. When somewhat more than the calculated amount of acid has been absorbed, the whole fluid becomes for a moment turbid and presently becomes clear again; only in one instance a small mass of crystals was observed opposite the delivery-tube. Dry carbonic acid led through the solution at —12° carried off ethyl chloride, and the residue was again chlorformanilide. When hydrochloric acid is passed into 1 gram phenyl isocyanate dissolved in 2.7 grams abso-

lute ether, no turbidity can be observed at any stage in any part of the liquid. The experiments repeated with modified proportions gave the same results. As in the case of ethyl anilidochlorformate ethyl chloride is formed, we led hydrochloric acid charged with ethyl chloride into a solution of 1 gram phenyl isocyanate in 2.5 grams ether. The presence of the ethyl chloride apparently made no difference, as the solution never showed signs of becoming milky. On adding 1 gram ethyl chloride to a like solution of phenyl isocyanate in ether charged with 3 to 4 equivalents of acid, no change was produced. These experiments seem to show that at the first entrance of hydrochloric acid into the ethereal solution of ethyl anilidochlorformate a substance is formed different from chlorformanilide, but yielding this compound almost at once even at —15° by loss of ethyl chloride. The only substance answering this description is the addition-product $C_6H_5.NH.CCl_2OC_2H_5$. We shall try to isolate such a product from similar ethers, as the methyl or amyl derivative. Its formation is also indicated by the fact that identical products result from the decomposition of ethyl anilidochlorformate with hydrochloric acid and of phenylurethane with phosphorus pentachloride, in connection with the action of the latter on other ethers and amides.

The remarkable ease with which ethyl chloride is split off when hydrochloric acid acts on ethyl anilidochlorformate, and the probability that it is due to the formation of a compound $C_6H_5.NH.C\begin{matrix}/Cl\\—Cl\\\backslash OC_2H_5\end{matrix}$, seem to us of especial importance in view of the large number of hitherto unexplained reactions in which a similar decomposition is observed. Such addition-products seem to vary exceedingly in stability. The imidoethers[1] $R.C\begin{matrix}=NR\\\backslash OR\end{matrix}$ form compounds with hydrochloric acid which have hitherto been considered as salts, $R.C\begin{matrix}=NR.HCl\\\backslash OR\end{matrix}$. Most of the reactions are much more easily explained by the constitution $R.C\begin{matrix}/NHR\\—Cl\\\backslash OR\end{matrix}$. Thus, on heating they lose ethyl chloride and form acid amides. This appears simple enough when represented thus:

[1] Pinner: Ber. d. chem. Ges. **10**, **11**, **16**, **17**, etc.

$$R.C\begin{cases}NHR\\ Cl\\ O\,C_2H_5\end{cases} = R.CO.NHR + ClC_2H_5,$$ but is difficult to explain by the salt-theory. Formic imidoether chlorides give with alcohols orthoformic ethers:

$$R.C\begin{cases}NHR\\ Cl\\ OC_2H_5\end{cases} + HOC_2H_5 + HOC_2H_5 = R.C\begin{cases}OC_2H_5\\ OC_2H_5\\ OC_2H_5\end{cases} + NH_2RCl.$$

Acetic anhydride reacts only with the free imido ethers and gives then diacetyl-amides and acetic ether.[1] Here there is evidently preliminary addition of acetic anhydride:

$$R.C\begin{cases}NH\\ OR\end{cases} + O\begin{cases}COCH_3\\ COCH_3\end{cases} = R.C\begin{cases}NHC_2H_3O\\ O-COCH_3\\ OR\end{cases} =$$

$$R.C\begin{cases}NHC_2H_3O\\ O\end{cases} + CH_3COOR.$$

The chief reaction on which the view of the salt-like nature of the hydrochloric-acid addition-product rests consists in the formation of double salts with platinic chloride. It seems not impossible that other chlorides can unite with platinic chloride. We hope soon to bring further experimental evidence bearing upon the constitution of the imidoether chlorides. Analogous substances in which the imido group is replaced by other radicles behave in the same way—for instance, ethyl benzhydroxamic acid,[2] $R.C\begin{cases}NOH\\ OC_2H_5\end{cases}$, forms with hydrochloric acid a derivative $C_6H_5.C(NOH)(OC_2H_5).HCl$, which, on warming moderately, yields ethyl chloride and benzhydroxamic acid. Dialkyl dichlorglycolates,[3] $(C_2H_3O)Cl_2.C.COOC_2H_5$, split on heating into alkyl chloride and alkyl oxalic chlorides:

$$(C_2H_3O)Cl_2.C.COOC_2H_5 = ClC_2H_5 + ClO.C.COOC_2H_5.$$

The main importance of the subject is in its application to esterification and saponification by halogen acids:

$$R.COOH + HCl + HOC_2H_5 = R.C\begin{cases}OH\\ Cl\\ OH\end{cases} + HOC_2H_5 =$$

$$R.C\begin{cases}OH\\ OC_2H_5\\ OH\end{cases} + ClH;$$ and

[1] Pinner: Ber. d. chem. Ges. **25**, 1434. [2] Lossen: Ann. Chem. (Liebig) **252**, 213.
[3] Anschütz: *Ibid.* **254**, 14.

$$R.COOC_2H_5 + HCl + HOH = R.C\begin{matrix}OH\\Cl\\OR\end{matrix} + HOH =$$

$$R.C\begin{matrix}OH\\OH\\OR\end{matrix} + HCl;$$

would lead to identical ortho-derivatives which would lose water or alcohol or some of both according to the proportion of alcohol or water within the sphere of action. If no water is present the esters yield alkyl halide and acid:[1]

$$R.C\begin{matrix}O\\OR\end{matrix} + HX = R.C\begin{matrix}OH\\X\\OR\end{matrix} = R.COOH + RX.$$

CHICAGO, *November* 29, 1893.

[1] Crafts: Compt. rend. **56**, 707; Gal: *Ibid.* **59**, 1049; Sapper: Ann. Chem. (Liebig) **211**, 168; Lippert: *Ibid.* **276**, 148.